NOV 1 1935

Vol. 21 OCTOBER, 1935 No. 144

JOURNAL OF THE INSTITUTION OF PETROLEUM TECHNOLOGISTS

FOUNDED 1913——INCORPORATED 1914

CONTENTS

	PAGE
Institution Notices	I–VIII
The Viscosity and Stability of Drilling Fluid. C. W. Woolgar, B.Sc., A.I.C.	825
The Explosion of Mixtures of Combustible Gases with Air. R. O. King, M.A.Sc., and George Mole, B.Sc., A.R.C.S., D.I.C.	838
A Wide Range Boiling-Point Conversion Chart for Hydrocarbons and Petroleum Products. E. S. L. Beale and P. Docksey	860
Treatment of Water for Domestic Purposes in a Trinidad Oil-Field. A. H. Richard, A.C.G.I., B.Sc., A.M.Inst.C.E.	871
Cyclic Constituents of Petroleum Ceresin. Jacob Müller and S. Pilat	887
The Coking of Petroleum Residues. D. Glynn Jones, M.Sc., M.Am.Assoc.Pet.Geol.	895
Abstracts	349a
Book Reviews and Books Received	386a

Published by The Institution of Petroleum Technologists, Aldine House, Bedford Street, Strand, London, W.C. 2, and Printed in Great Britain by R. Clay & Sons, Ltd., Bungay, Suffolk.

PRICE 7s. 6d.

All rights of Publication or Translation are reserved.

ANNOUNCEMENT

FOSTER WHEELER LTD.

HAVE PLEASURE IN ANNOUNCING
THAT THEY HAVE BEEN GRANTED SOLE
SELLING RIGHTS IN EUROPE FOR THE

SEPARATOR - NOBEL HEAVY SOLVENT DEWAXING PROCESS

AMONG THE MANY ADVANTAGES OF THE **SEPARATOR-NOBEL** HEAVY SOLVENT DEWAXING PROCESS, THE FOLLOWING ARE THE MOST PROMINENT:-

- **LOW FIRST COST**
- **LOW OPERATING COST**
- **NO FIRE HAZARD**
- **EQUALLY SUITABLE FOR HIGH AND LOW WAX CONTENT OILS WHETHER ACID TREATED OR NOT**
- **PARAFFIN OR MIXED BASE DISTILLATES AND RESIDUES DEWAXED**

REFINERIES INTERESTED IN DEWAXING PROBLEMS SHOULD ADDRESS ENQUIRIES TO:-

FOSTER WHEELER LTD.
ALDWYCH HOUSE,
LONDON, W.C. 2

Kindly mention this Journal when communicating with Advertisers.

G

E INSTITUTION OF PETROLEUM TECHNOLOGISTS

List of Officers, 1935–1936.

Past-Presidents:

Sir Boverton Redwood, Bart., D.Sc., F.R.S.E. (1914–1916).
Prof. Sir John Cadman, G.C.M.G., D.Sc., Hon. LL.D., Hon.D.Eng. (1916–1917).
The Rt. Hon. Lord Greenway of Standridge Earle (1917–1919).
Sir Frederick W. Black, K.C.B., B.A. (Lond.) (1919–1921).
Prof. John Samuel Strafford Brame, C.B.E., F.I.C., F.C.S. (1921–1923).
Herbert Barringer, M.Inst.C.E., M.I.Mech.E., M.I.N.A., M.Inst.Mar.Eng. (1923–1925).
Sir Thomas H. Holland, K.C.S.I., K.C.I.E., D.Sc., F.R.S. (1925–1927).
Alfred C. Adams (1927–1929).
A. E. Dunstan, D.Sc., F.I.C., F.C.S. (1929–1931).
James Kewley, M.A., F.I.C., F.C.S., M.I.Chem.E. (1931–1933).
T. Dewhurst, A.R.C.Sc., F.G.S. (1933–1935).

President:

Prof. Sir John Cadman, G.C.M.G., D.Sc., Hon. LL.D., Hon.D.Eng.

Vice-Presidents:

Lt.-Col. S. J. M. Auld, O.B.E., M.C., D.Sc.
Ashley Carter, A.M.I.Mech.E.
C. Dalley, M.I.E.E.
Prof. A. W. Nash, M.Sc., F.C.S., M.I.Mech.E.
J. McConnell Sanders, F.I.C., F.C.S.
F. B. Thole, D.Sc., F.I.C., F.C.S.

Members of Council:

G. H. Coxon.
A. Frank Dabell, M.I.Mech.E.
Arthur W. Eastlake, M.I.Min.E., A.M.I.Mech.E.
Elliott A. Evans, F.C.S.
F. H. Garner, Ph.D., M.Sc., F.I.C.
T. R. H. Garrett, M.A., F.G.S.
W. E. Gooday, A.R.S.M., D.I.C., M.Inst.M.M.
A. C. Hartley, A.C.G.I., M.Inst.C.E., M.I.Mech.E.
Prof. V. C. Illing, M.A., M.Inst.M.M.
J. S. Jackson, B.Sc., A.I.C.
E. R. Redgrove, Ph.D., B.Sc., F.C.S.
James Romanes, M.A., F.G.S.
A. Beeby Thompson, O.B.E., M.I.Mech.E., M.Inst.M.M., F.G.S.
A. Wade, D.Sc., A.R.C.S., F.G.S., M.Inst.M.M., F.Am.G.S.
Cecil W. Wood, F.I.C.

* Deceased.

Chairmen of Committees of Council :

Awards : The President.
Benevolent Fund : A. E. Dunstan, D.Sc., F.I.C., F.C.S.
Branch : T. Dewhurst, A.R.C.Sc., F.G.S.
Cancer Research : J. Kewley, M.A., F.I.C., F.C.S., M.I.Chem.E.
Chemical Standardization : Prof. J. S. S. Brame, C.B.E., F.I.C., F.C.S.
Election : J. McConnell Sanders, F.I.C., F.C.S.
Engineering Standardization : Lt.-Col. S. J. M. Auld, O.B.E., M.C., D.Sc.
Finance : C. Dalley, M.I.E.E.
House : Arthur W. Eastlake, M.I.Min.E., A.M.I.Mech.E.
Library : James Romanes, M.A., F.G.S.
Publication : A. E. Dunstan, D.Sc., F.I.C., F.C.S.
Research Fund : J. Kewley, M.A., F.I.C., F.C.S., M.I.Chem.E.

Chairmen of Branches :

Persia : E. C. Brewster.
Rumania : P. R. Clark.
Trinidad : Commander H. V. Lavington, R.N.
South Wales : W. C. Mitchell, B.Sc., M.Inst.C.E., M.I.Mech.E.
Burma : G. W. Lepper, B.Sc., F.G.S.

Chairmen of Students Section :

London Branch : A. S. Bridgwater.
Birmingham Branch : E. R. Ward.

Honorary Treasurer :
Lord Plender of Sundridge, G.B.E.

Solicitors :
Messrs. Ashurst, Morris, Crisp & Co.

Auditors :
Messrs. Price, Waterhouse & Co.

Bankers :
Westminster Bank, Limited.
21, Lombard Street, London, E.C. 3.

Hon. Editor :
A. E. Dunstan, D.Sc., F.I.C., F.C.S.

Associate Editor, Librarian and Secretary, Standardization Committee:
George Sell.

Hon. Secretary :
Arthur W. Eastlake, M.I.Min.E., A.M.I.Mech.E.

Secretary :
S. J. Astbury, M.A., A.M.Inst.C.E

Offices—Aldine House, Bedford Street, Strand, London, W.C. 2.
Telegrams : Instpetech, Lesquare, London.
Telephone : Temple Bar 1842.

NOTICES.

The Institution as a body is not responsible for the statements of opinion expressed in any of its publications.

Copyright.—Publication of abstracts of Papers and articles appearing in the Journal is permitted, provided that acknowledgment is made to the Institution of Petroleum Technologists.

Papers and Articles.—The Council invites Papers and Articles both for reading at Ordinary Meetings of the Institution and for publication in the Journal. All Papers, whether for reading or publication, will be submitted to a referee appointed by the Publication Committee.

The Institution has published a brochure "Instructions for the Guidance of Authors" containing details of recommended practice in the preparation of Papers for publication. Copies of this brochure will be supplied on request.

Pre-Prints.—Advance proofs of Papers to be read at Ordinary Meetings are generally available about a week before the Meeting. Members wishing to be supplied with these pre-prints are requested to notify the Secretary.

Abstracts.—Members and Journal Subscribers desirous of receiving the Abstracts printed on one side of the paper only, can be supplied with these at a charge of 10*s.* per annum per copy, payable in advance.

Issue of Journal.—Members whose subscription is not in arrear receive the Journal free of cost. A member whose subscription is not paid by March 31st of the year for which it is due is considered to be in arrear.

Changes of Address.—Members are requested to notify any change of address to the Secretary.

Benevolent Fund.—The Benevolent Fund is intended to aid necessitous persons who are or have been members of the Institution, and their dependent relatives.

The Fund is raised by voluntary annual subscriptions, donations, and bequests, and all contributions should be sent to the Secretary of the Institution at Aldine House, Bedford Street, London, W.C. 2. The Fund is administered by the Council through the Benevolent Fund Committee, and all applications in connection therewith must be made on a special form which can be obtained from the Secretary of the Institution.

Appointments Register.—A register of members requiring appointments is kept at the offices of the Institution, and every effort is made to assist members of the Institution in search of employment.

Members who desire their names and qualifications to be included in this register are requested to apply to the Secretary for the Form of Application for Registration, if they have not already done so. Members residing in the London area are asked, if possible, to return this Form in person and make themselves known, together with their requirements, to the Secretary. It is also requested that members should notify the Secretary immediately they have obtained an appointment.

In submitting names of candidates to prospective employers it is understood that the Institution accepts no responsibility and gives no guarantee.

Library.—The Institution's Library may be consulted between the hours of 9.30 a.m. and 5 p.m. daily. (Saturdays, 9.30 a.m. to 12 noon.)

NOMINATIONS FOR MEMBERSHIP.

The following nominations for membership of the Institution of Petroleum Technologists were approved by the Council on 8th October, 1935, and the application forms may be seen at the offices of the Institution.

The names of the Proposer and Seconder are given in parentheses.

As Members.

BEGG, Alfred John, Research Engineer, c/o L. Gardner & Sons, Barton Hall Engine Works, Patricroft, Manchester. (W. H. Goddard; A. E. Dunstan.)

BORWICK, Henry Barton, Engineer, 4, Wimbledon Avenue, St. Kilda, S. 3, Victoria, Australia. (R. W. Dunster; A. R. Code.)

DEMOULINS, Henry Dieudonne, Refinery Superintendent, Agwi Petroleum Corpn., Fawley, Hants. (F. H. Garner; A. Hamilton.)

FENSKE, Merrell Robert, Prof. Petroleum Refining Lab., Pennsylvania State College, State College, Pa., U.S.A. (G. Egloff; S. R. Wilson.)

HERRING, Percy Henry, Engineer, Penrose, 15, Seymour Road, East Molesey, Surrey. (S. J. M. Auld; A. E. Dunstan.)

HOLLEY, Alfred Ewart, Refinery Works Manager, Cefn Lodge, Cefn Parc, Skewen, Glamorgan. (A. E. Dunstan; G. H. Coxon.)

LAMB, Maurice Frederic, Research Chemist and Engineer, 6, Marlboro' St., Mt. Albert, Auckland, S.W. 1, New Zealand. (W. L. Barr; L. F. Elsby.)

MACKIE, William Frederick Charles, Chemist, Apartado 161, Tampico, Tamps, Mexico. (J. McConnell Sanders; W. Webber.)

MALHERBE, Gideon John, Manager, Petroleum Division, De Laval Separator Co., 165, Broadway, New York. (A. G. Marshall; J. Kewley.)

SWANSON, Harry Robert, Engineer, 220, East 42nd Street, New York. (C. H. Edmonds; A. E. Dunstan.)

THORNBURY, William Madison, Drilling Superintendent, c/o B.O.D. Co., Ltd., Mosul, Iraq. (Ashley Carter; A. W. G. Bleek.)

TILLMANN, Richard, Engineer, Wassenaarscheweg 20, The Hague, Holland. (H. van der Waerden; I. J. F. Reydon.)

As Associate Members.

EDWARDS, Stanley Haines, Chemist, c/o Shell Co. of N.Z. Ltd. Laboratory, Hutt Road, Wellington, New Zealand. (L. F. Elsby; M. L. H. Stewart.)

GARDINER, Russell Doverdale Campbell, Chemist, 931, Dominion Square Building, Montreal, Canada. (R. H. Sperling; E. Coste.)

HEARN, Harold Edwin, Topping Plant Superintendent, c/o Trinidad Leaseholds, Ltd., Pointe-a-Pierre, Trinidad, B.W.I. (B. G. Banks; A. G. V. Berry.)

POTTER, Joseph Peach, Production Superintendent, c/o Apex (Trinidad) Oilfields, Fyzabad, Trinidad, B.W.I. (G. H. Scott; H. D. Fletcher.)

SCHNEIDER, Frederick John, Lubrication Engineer, 40, Southfield Road, Bricknell Avenue, Hull. (R. G. Stickland; W. E. Gooday.)

SUNDSTROM, Richard Fleming, Technical Assistant & Secretary, Svenska Petroleum AB. Standard, Nybrogatan 6, Stockholm. (F. H. Garner; N. Backlund.)

As Transfer to Associate Members.

BLACKWELL, William, Lubricating Oil Manufacturer, Victoria Oil Works, Aston, Birmingham. (W. H. Howe; A. W. Nash.)

DARLEY, Henry Cecil Hastings, Geologist, Apex (Trinidad) Oilfields, Siparia P.O. Trinidad, B.W.I. (G. H. Scott; H. C. B. Hickling.)

LEENDERTSE, Jacob Jan, Chemical Engineer, Hugo de Grootstraat 148, Delft, Holland. (H. I. Waterman; W. J. Hessels.)

PERKS, Angus John, Chemist, c/o Iraq Petroleum Co., Kirkuk, Iraq. (L. V. A. Fowle; G. Heseldin.)

SWEETLAND, Leslie Benjamin, Engineer, c/o C.P.I.M., Ammastad, Curacao, D.W.I. (B. Gluckman; Peter Kerr.)

WOOLGAR, Cedric Warren, Research Fellow, The Oil Dept., University of Birmingham, Edgbaston, Birmingham. (A. W. Nash; L. V. W. Clark.)

As Students.

HAZZARD, Geoffrey Francis, Chemist, 216, Pavilion Road, Sloane Square, S.W. 1. (J. S. Jackson; J. Parrish.)

PARR, Ronald Walter, Chemical Assistant, 52, Cambridge Road, Teddington, Middlesex. (J. S. Jackson; J. Parrish.)

PRIESTLEY, Samuel Albert Gaston, Technical Assistant, The Grove, Roseville, New South Wales, Australia. (D. Fell.)

SLADE, Henry Martin, Engineer, 85, Pendle Road, Streatham, S.W. 16. (W. E. Gooday; G. Sell.)

As Associates.

BUCKERIDGE, Bernard Charles Jackson, Fire Engineer, Municipal Fire Bridge, Singapore, S.S. (L. H. Cooper; K. S. Ananthanarayanan.)

WHITE, Reginald Christopher, Divisional Superintendent, 241, Eastern Avenue, Ilford, Essex. (W. B. Heaton; J. F. F. McQueen.)

APPLICATION FORMS FOR ADMISSION.

The Council desire to direct the attention of members who Propose or Second an Application Form for admission to the Institution to the importance of sending a covering letter for the guidance of the Election Committee.

COAL HYDROGENATION.

The Council of the Institute of Fuel extends a cordial invitation to the members of the Institution of Petroleum Technologists to attend the presentation of a Paper by Mr. Kenneth Gordon entitled "The Development of Coal Hydrogenation by the Imperial Chemical Industries Ltd."

This Paper will be presented in the Lecture Theatre of the Institution of Electrical Engineers, on Friday, 22nd November, at 6 p.m. The meeting will be an open one, and no tickets of admission will be required.

It is hoped that advance copies of the Paper will be available about ten days previous to the meeting.

STUDENTS' SECTION (LONDON BRANCH).

The Annual Open Meeting of the Students' Section, London Branch, will be held on Tuesday, 19th November, at the Sir John Cass Technical Institute, Jewry Street, Aldgate, E.C. 3, at 6 p.m.

Mr. J. B. Aug. Kessler (Director, Royal Dutch-Shell Group) will give an address on "The Petroleum Industry and the World Crisis."

Junior members of the staffs of oil companies are particularly invited, whether Students of the Institution or not.

NOMINATIONS FOR COUNCIL.

Members are reminded that in accordance with the By-Laws Nominations for Council must be in the Secretary's hands not later than 30th November next. Nomination Forms may be obtained from the Secretary.

ASSOCIATED STUDENTS.

In order to enable junior employees of petroleum companies to participate in the activities of the Students' Section of the Institution, the Council has approved "Associated Students" of this Section.

Associated Students will be entitled to receive notices of and to attend meetings of the Students' Section, and to make use of the Institution Library. They will not receive the *Journal*, and will not be eligible for Students' Prizes.

The subscription of an Associated Student is 7*s*. 6*d*. per annum, which should be paid to the Honorary Secretary, Students' Section (London Branch), Mr. B. C. Ferguson, St. Helens Court, Great St. Helens, London, E.C. 3.

There is at present no age limit for Associated Students, but they will be required to proceed to Student or other grade of Membership (according to age) before the expiry of two years from the date of their becoming Associated Students.

ARTHUR W. EASTLAKE.
Honorary Secretary.

PERSONAL NOTES OF MEMBERS AND SPECIAL NOTICES.

It is suggested that members send information regarding their movements to the Secretary for insertion under this heading.

Mr. T. J. F. ARMSTRONG has returned to Burma.

Mr. J. L. BENARD is now in Burma.

Mr. C. A. MOON has left Venezuela and is now in Trinidad.

Mr. J. GOVAN SMILLIE has returned to Venezuela.

Mr. E. G. STIBBS has left for Trinidad.

Mr. P. VON WEYMARN is in Canada.

The Secretary would be glad to learn of the addresses of the following members: A. MACLEAN, W. W. PEARCE, K. A. SPEARING and A. C. VIVIAN.

BRANCH NOTES.

The Trinidad Branch of the Institution is holding its Fifth Annual Dinner at the Queens Park Hotel, Port-of-Spain, Trinidad, on Saturday, 26th October.

The opening meeting of the 1935–36 Session of the Rumanian Branch was held at Ploesti on Friday, 4th October. A Paper was read by Mr. D. I. Maxwell, B.A., B.Sc. (Chem. Eng.), Refinery Manager of the Romano-Americana Company on "A Review of Recent Advances in Petroleum Processes."

PROCEEDINGS, WORLD PETROLEUM CONGRESS, 1933.

A limited number of the Sectional Volumes of the Proceedings of the World Petroleum Congress are now available at reduced prices. These can be obtained from the offices of the Institution at the prices indicated below :

Vol. A. Geological Significance of the Regional Distribution of Oilfields. Pp. 82. 2*s.* 6*d.*

Vol. B. Modern Developments in Geological Exploration. Pt. I, Geophysics. Pp. 112. 2*s.* 6*d.*

Vol. C. Modern Developments in Geological Exploration. Pt. II, Aeroplane Reconnaissance and Photography, Evaluation of Surface Evidences of Petroleum, Field Methods : Geological Aspects of Oilfield Development. Pp. 154. 3*s.* 6*d.*

Vol. D. Production Section : Drilling, Production, Transport and Storage. Pp. 206. 5*s.* 0*d.*

Vol. E. The Refining of Cracked Gasolines and the Use of Inhibitors for Gum Prevention; Determination of Gum in Gasoline; Knock-Rating; Fuels for High-Speed Compression-Ignition Engines, their Qualities and Method of Knock-Rating. Pp. 280. 5*s.* 0*d.*

Vol. F. Hydrogenation; Extraction Processes for the Refining of Oil; Lubricating Oil; Viscosity and Its Expression. Pp. 264. 5*s.* 0*d.*

Vol. G. Bituminous Materials; Bituminous Emulsions. Pp. 148. 3*s.* 6*d.*

Vol. H. Kerosine; Alternative Fuels; Oil–Coal Fuels; Petroleum as a Chemical Raw Material. Pp. 172. 2*s.* 6*d.*

Vol. I. Measurement of Oil in Bulk; Nomenclature from the Legal Aspect; International Co-operation in Standardization; "Science in the Petroleum Industry," by Sir John Cadman; "Rationalization of the Oil Industry," by Mr. J. B. Aug. Kessler; Report of the Final Session; Speeches at the Congress Banquet. Pp. 82. 1*s.* 0*d.*

OBITUARY.

Arthur D. Little.

Born in 1863, educated at Berkeley School, New York, and the Massachusetts Institute of Technology, Arthur D. Little joined the Richmond Paper Company of Rhode Island as a chemist in 1884. Two years later he joined with R. B. Griffen in the foundation of a consulting industrial chemical laboratory. At that time there was little published technical information available for the paper industry, and their book, "The Chemistry of Paper Making," was accepted as the principal authority on that subject for over thirty years.

His book on paper-making was followed by many papers and published addresses, and these helped to inspire many others to go forward in research into new fields.

He was President of the American Chemical Society 1912 to 1914 and of the American Institute of Chemical Engineers in 1919, and during these terms of office was responsible for changes and studies of major importance. He was also the originator of the School of Chemical Engineering Practice at the Massachusetts Institute of Technology.

He joined the Institution of Petroleum Technologists in 1923 and remained a Member until the time of his death on Aug. 1st, 1935.

STUDENTS' SECTION (LONDON BRANCH).

Programme for 1935.

Monday, 14th October.

Meeting—**"Value of Research in the Petroleum Industry."** Dr. A. E. Dunstan (Past-President).

Tuesday, 24th October.

Visit—The works of Messrs. George Kent, Ltd., Luton.

Tuesday, 5th November.

Meeting—**History and Development of Tankers.** Mr. Brian Orchard Lisle (Student).

Tuesday, 19th November.

Annual Open Meeting: **"The Oil Industry and the World Crisis."** Mr. J. B. Aug. Kessler (Joint Managing Director, Royal Dutch-Shell Group).

Tuesday, 3rd December.

Meeting—**"The Action of Certain Natural and Treated Earths upon Petroleum and its Products."** Mr. H. T. Lorne, B.Sc., A.R.C.S. (Student).

Tuesday, 17th December.

Meeting—**Political and Economic Geography of Burma, India and the East Indies.** Dr. L. Dudley Stamp (Member).

THE VISCOSITY AND STABILITY OF DRILLING FLUID.*

By C. W. Woolgar, B.Sc., A.I.C.

Synopsis.

The viscosity and stability of some drilling muds have been studied, and it is shown that yield point and viscosity must be differentiated and that yield point is the important criterion of a mud.

The density of the bottom portions of a settled mud were found to be independent of the length and diameter of the column, and therefore the stability of a mud is not so important as has hitherto been supposed.

The calibration and use of a Stormer viscometer are also described.

Although some millions of pounds are spent annually on drilling fluid equipment and raw material, and its accurate control is essential for successful drilling, there is still a divergence of opinion as to the optimum values of its various properties for a given drilling problem, and a corresponding divergence in the methods used to measure those properties. The most important are its density, its viscous state and its stability, and it is proposed to suggest, and discuss in some detail, a standard method for measuring these quantities, particularly the viscous state and the stability, which will give useful and practical information to the driller.

Four samples of clay were used in the various experiments—viz. a Kamilal shale from Attock, India, two Pontic clays from Rumania, one from the Ceptura and one from the Piscuri field, and a Trinidad clay. All were samples of actual drilling clay, the Kamilal shale arriving as a 95 lb. per cubic foot mud, straight from the well.

Density determinations need no special mention, as the usual field's method of weighing a previously calibrated bucket filled with the mud, or even a tin container on a cheap balance, gives sufficiently accurate results. Care should be taken, however, to see that the receptacle is clean before each weighing, and that it is recalibrated each time it is dented, as cases have been known where workmen have continued using a metal container dented almost out of recognition, although the original volume calibration was still employed.

A short series of experiments was carried out to see if the density of a mud, calculated from the density of the clay in the dry state, and the quantities of clay and water used, differed from the experimentally determined density. The results given below were obtained using a Kamilal shale

Clay, per cent.	Calculated Density	Found Density.
20·73	1·149	1·150
28·42	1·217	1·226
37·74	1·313	1·318
43·91	1·385	1·385
47·13	1·424	1·422
52·95	1·513	1·504

* Paper received March 25th, 1935.

clay from India of density 2·734, and it will be seen that the difference, for this particular clay, at any rate, is negligible from the field engineer's point of view.

Viscosity.

The viscosity is the next important quantity, and this presents a far more complicated problem than the simple density determinations. The commonest viscometers used on the field are of the orifice type: although these are simple, and can give good results when used on a true liquid such as an oil, they will give very misleading results when used to measure the viscous state of such a colloidal system as a drilling fluid. The viscometer used in the present work was a Stormer, an instrument which is rapidly gaining favour in the oil industry, and by means of which a true measure of the viscous state of a drilling mud may be obtained. This instrument is of the concentric cylinder type, and although of robust construction, needs care in handling, as the calibration constants will be altered if it is even slightly damaged. For use with colloids the calibration is rather laborious, and a few words on the subject may not be out of place here. The makers recommend that the times for 100 revolutions of the cup be taken for various solutions of known viscosity, using the 100-gram weight supplied with the instrument, and from this a calibration chart of viscosity against time per 100 revolutions may be constructed. Unfortunately, mud fluids, in common with most colloidal systems, vary their apparent viscosity with the rate of shear used, and for a full description of the viscous state of the mud it is necessary that their viscosity should be measured at several shearing rates: for rough comparative purposes a single determination will suffice, but it must be carried out at an agreed shearing rate—*i.e.* the weights must be varied to obtain a given time per 100 revolutions of the cup. Nine glycerol solutions, the viscosity of which had been determined from the density/viscosity relations given in the International Critical Tables, were used and the times per 100 revolutions found for various driving weights: the mean of twenty observations was taken for each weight and the whole calibration was carried out at 20° C. From this data a "revolutions per minute/driving weight" curve could be drawn for each solution, and from these curves two series of calibration curves were obtained —viz. a "viscosity/time per 100 revolutions for a fixed weight" and a "viscosity/weight causing a given number of revolutions per minute." The first series was used for a detailed investigation of the viscous state of the mud at various shearing rates, and the second series, of which a single curve only was drawn, for 600 revolutions per minute, was used for taking viscosities according to the standard field method with a Stormer viscometer. A trial and error method is generally used on the field to determine the weight necessary to give 600 revolutions per minute of the cup, but a quicker and more accurate method is to use weights giving 100 revolutions in about 9·5 and also 10·5 seconds, and one can then intrapolate accurately to 10 seconds = 600 revolutions per minute.

It is axiomatic that shearing stress is proportional to shearing strain in a true fluid, and it was therefore to be expected that the "revolutions per minute/weight" curves for any given solution would be linear, but

this was found not to be the case (Fig. 1), although linearity was approached as viscosity increased and in a separate experiment with castor oil ($\eta = 986$ centipoises at 20° C.) a straight line was obtained. Friction in the instrument was corrected for by subtracting from the weights used the weight which would cause the noted rotation if no liquid was present, but linearity was still not obtained, the corrected curves being similar in all respects to the uncorrected ones shown in Fig. 1, but displaced slightly towards the shearing rate axis. It was presumed that the baffles were causing eddy currents which were affecting results, although it would be expected that such currents would decrease and not enhance the shearing

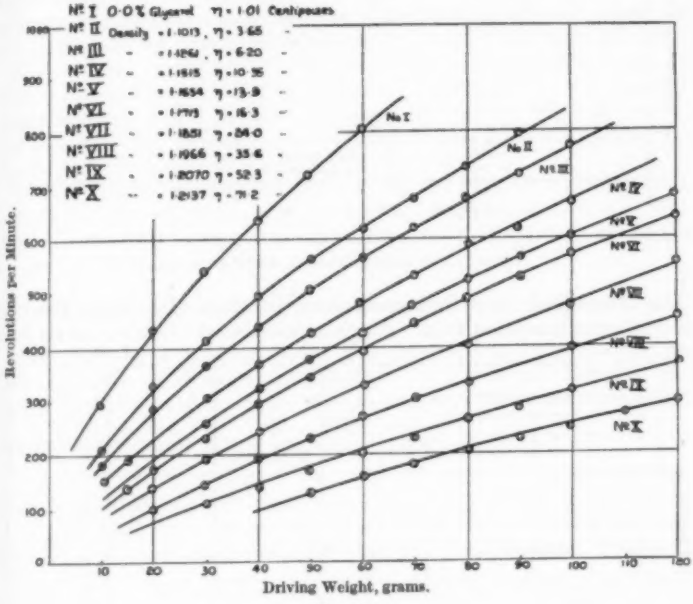

FIG. 1.

SHEARING RATE/SHEARING STRESS CURVES FOR THE GLYCEROL SOLUTIONS USED IN CALIBRATING THE STORMER VISCOMETER.

rates—*i.e.* the curves should be convex to the force axis and not to the shearing rate axis.

It was found that both the "viscosity/time per 100 revolutions" and the "viscosity/weight per given revolutions per minute" curves were linear above viscosities of about 5 to 6 centipoises, and it is therefore recommended that the Stormer should not be used for liquids of less than 6 centipoises viscosity.

Bingham,[1] in attempting to explain the anomalous viscosity of colloids, postulated a yield value or minimum shearing stress below which no flow could occur, and then a linear relation between shearing rate and applied force, giving a curve such as Fig. 2. The measured viscosity at the shearing

rate C is given by OC/OB in the appropriate units, whereas the actual viscosity is OC/XB + a yield point represented by OX.

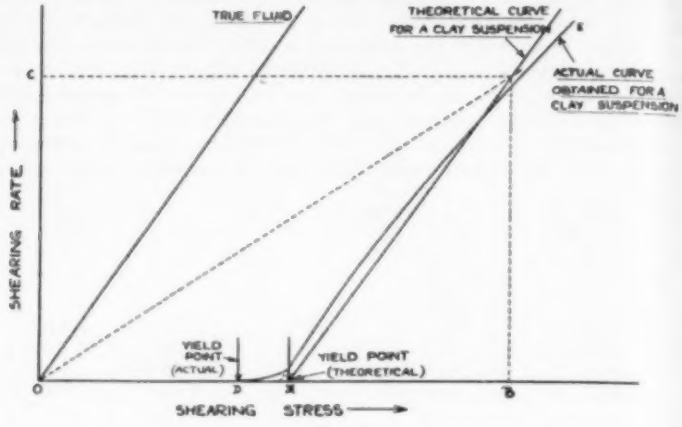

FIG. 2.

SHEARING STRESS/SHEARING RATE CURVES.

This theoretical curve has never been obtained, DE being the usual practical approximation to it. Bingham ascribes the flow at values below

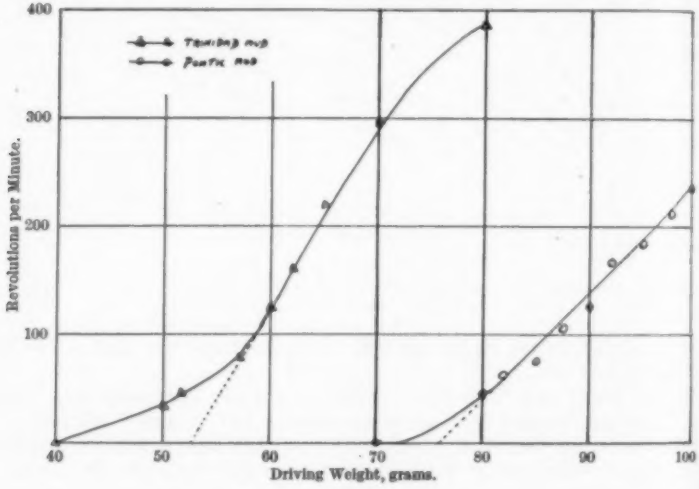

FIG. 3.

SHEARING RATE/SHEARING STRESS CURVES.

yield point intercept as due to "seepage," presumably of the dispersive phase around the disperse phase. Hatschek,[2] from some results on gelatin

sols and on starch suspensions, questions the existence of a yield point, and states that the shearing rate/stress curve in all cases passed through the origin: for viscous muds, however, there is no doubt at all of the existence of such a quantity, as results expressed in Fig. 3 show: these shearing rate/applied force curves were picked at random from a series done on various clays and show quite definitely a yield point: with the Trinidad clay of density 1·108, for instance, 50 grs. caused 35 revolutions per minute, whereas 40 grs. caused no movement in the cup even when left over-night. It must be realized that these clays differ from Hatschek's colloidal gelatin and starch preparations in that they are only partly colloidal, and contain a large number of particles outside the colloid range, and they could not, therefore, be expected to behave like pure colloids.

The shearing gradients both in the Stormer viscometer rotating at 600 revolutions per minute and in a typical drilling string can readily be calculated, and it will be seen that they are widely differing quantities, and therefore the measured viscosity may give little indication of the viscosity resisting flow in the drill pipe.

In the viscometer used the diameter of the rotating cup was 3·1 cm. and the clearance between the cup and the baffles was 0·15 cm. If the shearing rate is 600 revs. per min., then the speed of rotating cup surface is $\pi \times 3{\cdot}10 \times 10 = 97{\cdot}4$ centimetres/second.

$\therefore$ The velocity gradient is $\dfrac{974}{0{\cdot}15} = 650$ centimetres/second/centimetre.

Now, consider a 4½-inch, 16-lb. drill pipe drilling in an 8-inch casing with mud flow at 60 gallons/per minute. The internal diameter of the pipe is 4·388 in. = 15·12 sq. in. of cross section. The mud velocity in the pipe will therefore be $\dfrac{60 \times 1728}{60 \times 6{\cdot}24 \times 12 \times 15{\cdot}12} = 1{\cdot}53$ feet/second.

$= 46{\cdot}6$ centimetres per second.

If we assume that the layer of mud in contact with the drill pipe is stationary, and taking the maximum velocity, along the centre of the pipe, as approximately twice the mean velocity, we get the shearing gradient as $\dfrac{46{\cdot}6 \times 2}{2{\cdot}194 \times 2{\cdot}54} = 16{\cdot}7$ centimetres per second per centimetre.

By similar methods the gradient between casing and drill pipe comes to 23·8 centimetres/per second per centimetre.

The apparent viscosity on a Stormer, at these gradients, of a mud which had a viscosity of 10 centipoises at 600 revolutions per minute might be anything between 80 and 250 centipoises, and at such low gradients resistance to flow is governed by the yield point value, and not by the viscosity—see Fig. 2.

The horizontal shearing gradient at the rotational speed of the drill pipe is even less, being, for the case quoted above, of the order of 5 inverse seconds at 60 revolutions per minute, but it is the vertical motion with which we are concerned, as this governs pump pressures and the suspension of cuttings.

The possession of a marked yield point is exhibited only by the more viscous muds, 8 to 10 centipoises and over at 600 revolutions per minute, and thinner muds, which are frequently used in drilling, give stress/strain

curves which appear to go through the origin, but the viscosity still varies with the shear, although not so markedly, this being indicated by the pronounced curvature of the shearing rate/stress diagram. It is thus obvious that for viscous muds particularly, shear point values are of far more importance than viscosities at 600 revolutions per minute, or at any other arbitrary value; for, besides determining resistance to flow, the yield points govern the maximum size of particle which will be held in suspension if pumping stops. Meyer[3] has also reached a similar conclusion as to the importance of yield point and not viscosity in drilling muds, and in one example he shows that to overcome viscosity in a given length of 4-inch line may require from 18 to 33 lb. per square inch pump pressure, whereas

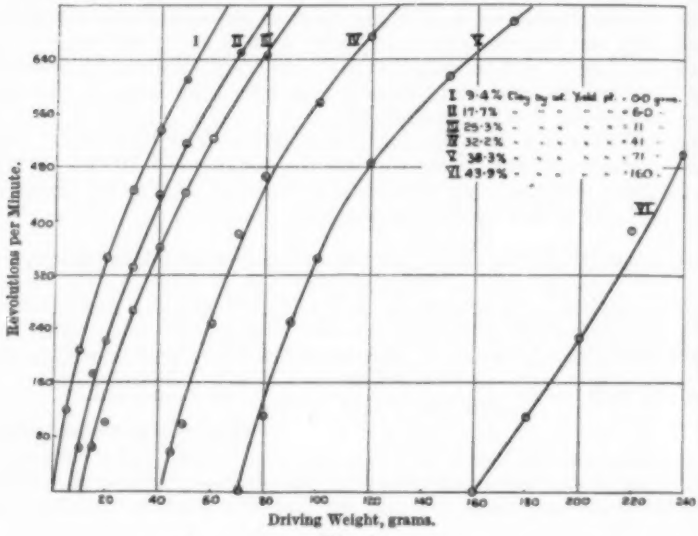

FIG. 4.

SHEARING STRESS/SHEARING RATE CURVES FOR MUDS OF VARYING CLAY CONCENTRATION.

to overcome the corresponding yield point in the mud may require from 57 to as much as 570 lb. per square inch pressure.

The relationship between density, viscosity and shear point was then studied by the author. Various muds were made by grinding samples of some Rumanian Pontic Clay for 1 hr. with water, and the shearing rate/applied force curves obtained (Fig. 4): the yield point was measured by the intercept of the curve on the stress axis, and was therefore the maximum driving weight on the viscometer which was just insufficient to cause rotation of the cup. On graphing the yield points obtained thus against the densities of the muds the interesting curve shown in Fig. 5 is given, which appears to be typical of all such systems.[4] Below 24 per cent. clay, corresponding to a mud of about 73 lb. per cubic foot, the yield point is negligible and the viscosity low, and it would be unsuitable for drilling,

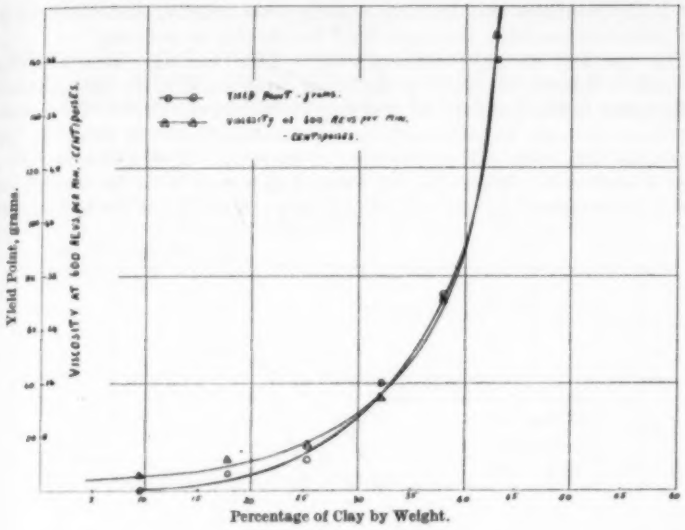
Yield Point, grams.
Viscosity at 600 revs per min. - centipoises.
Yield Point - grams.
Viscosity at 600 revs per min. - centipoises.
Percentage of Clay by Weight.

FIG. 5.

DENSITY/VISCOUS STATE CURVE.

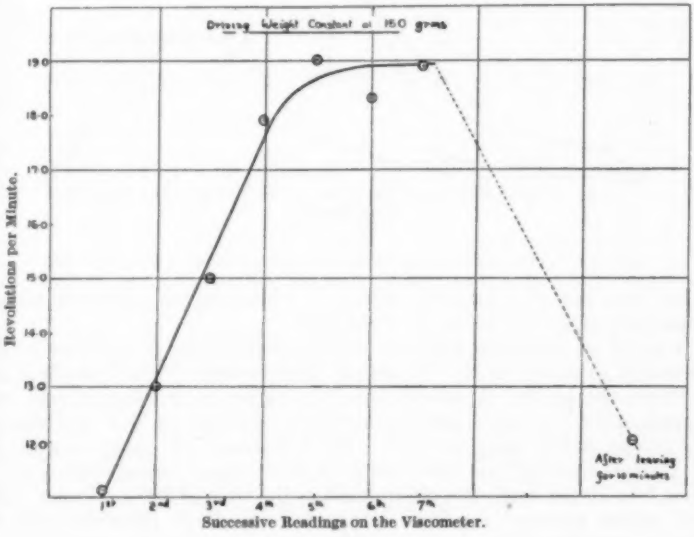
Drilling Weight Constant at 15.0 grms
Revolutions per Minute.
After leaving for 10 minutes
Successive Readings on the Viscometer.

FIG. 6.

VARIATIONS OF SHEARING RATE WITH SUCCESSIVE DETERMINATIONS OF "VISCOSITY."

but both quantities then increase rapidly with density, and about 82 lb. per cubic foot would be the upper limit for the clay in question.

The viscosity at 600 revolutions per minute was also measured (Fig. 5), and it follows the yield point curve very closely, so that although yield point is the property of real importance to the driller, the entirely arbitrary viscosity at 600 revolutions per minute does, in this case, give him some indication of the suitability of his mud. A shearometer such as that described by Meyer (*loc. cit.*) would, however, be a far simpler and cheaper instrument to use, and would give a measure of the actual yield

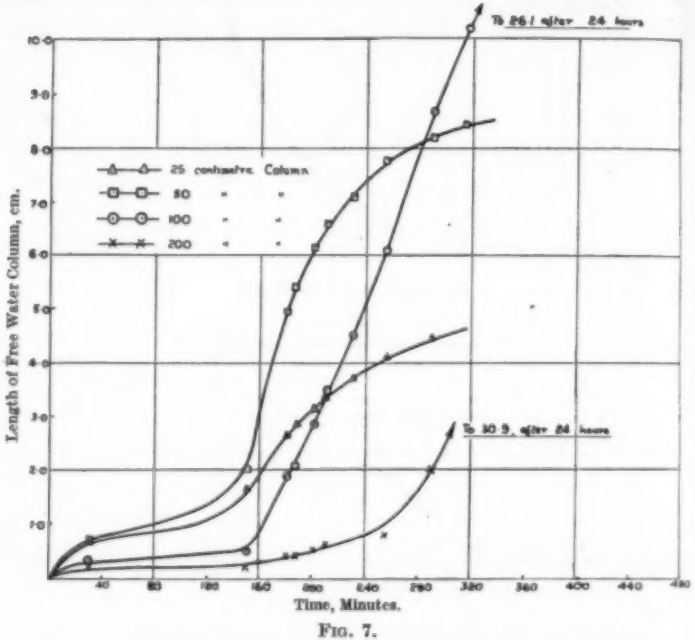

FIG. 7.

SETTLING RATE CURVES FOR TRINIDAD CLAY, INITIAL DENSITY, 1·070.

point, and not of a property which is related in an unknown though apparently close manner to the yield point.

A point of technique which is worth noting is the dependence of the measured viscosity on the immediate past history of the sample: this is illustrated by Fig. 6, which shows the variation of shearing rate, and consequently viscosity, during successive readings on the instrument, the driving weight being constant. This variation is, of course, exaggerated by the low shearing rate used, but even at the more normal rates a fall of from 5 to 10 per cent. was often noted in the time of 100 rotations of the cup before constant readings were obtained. It is therefore essential that all samples should be thoroughly agitated before measuring the viscosity, and readings should be repeated until they are constant to within 0·2 or 0·3 second.

Stability.

The stability, or its inverse quantity, the settling rate measures the tendency of a mud to form a sludge if pumping ceases. It is usually measured by the percentage of clear water appearing at the top of a mud column after a given time, generally 24 hours.

Strong,[5] advocating a standard method for measuring settling rates, says that there is reason to suppose that initial rates are independent of the length of column employed and therefore, for comparative purposes, the same length of column must always be used. It was decided to test

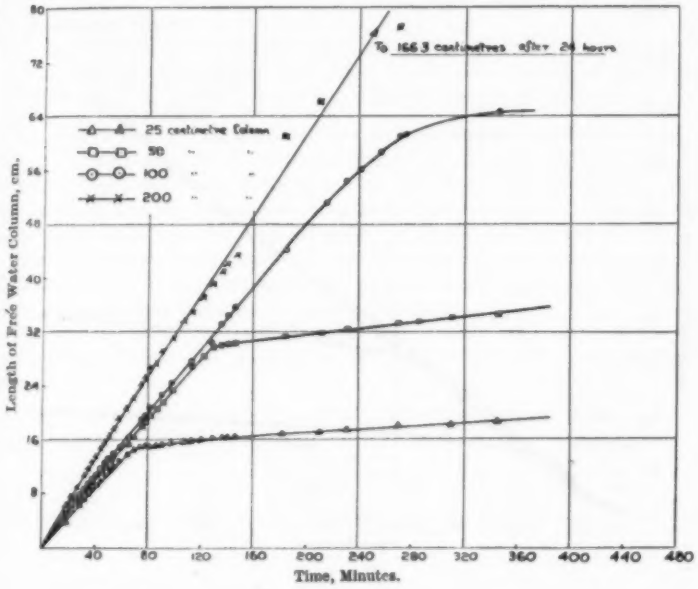

Fig. 8.

SETTLING RATE CURVES FOR A KAMILAL SHALE, INITIAL DENSITY, 1·081.

this statement and to suggest if possible a laboratory or fields method of measuring mud stability which would give information of the conditions at the bottom of the drill hole after pumping operations had ceased.

It was found that the diameter of the tube used had no effect on the settling rate. Tubes with diameters ranging from 0·6 to 4·8 centimetres were used, and within the limits of error of the experiment no difference could be detected in settling. In one typical run, the results of which are given below, the percentage settled in 24 hours was :—

Diameter of column, cm..	0·6	0·95	1·4	1·70	3·1	4·8
Per cent. settled in 24 hrs.	62	62·4	62·5	63	62·4	63·2

Finally a mud sample was settled in a beaker of 9·5 centimetres diameter and also in a 1·5-centimetre-diameter test tube, the initial column being 10 centimetres long, and after 24 hours the height of the mud column was 4·8 centimetres in the beaker and 4·7 centimetres in the test tube.

The effect of length of column was then investigated; four tubes of 25, 50, 100 and 200 centimetres length, fitted with draw-off taps at the bottom and six different clay suspensions, were used, the level of the mud/water surface being read every few minutes and the extremely interesting series of curves, of which Figs. 7 to 10 are typical, were obtained. It should be noted that the Kamilal shale clay possessed scarcely any

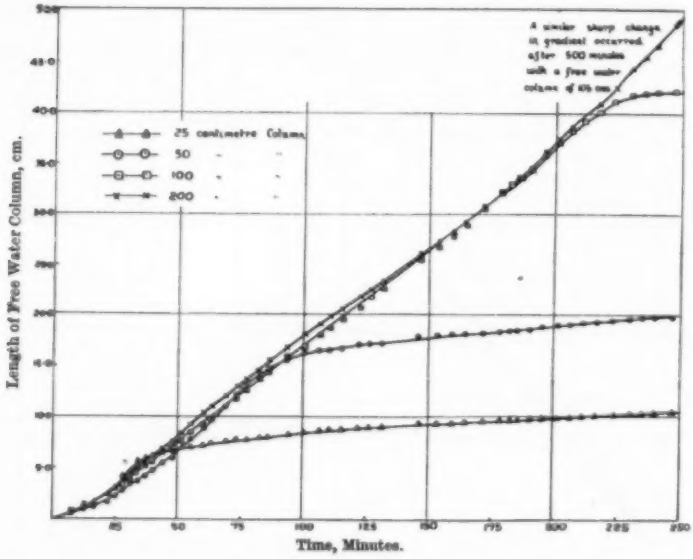
A similar sharp change in gradient occurred after 500 minutes with a free water column of 45 cms.
25 centimetre Column
50 " "
100 " "
200 " "
Length of Free Water Column, cm.
Time, Minutes.

FIG. 9.

SETTLING RATE CURVES FOR A PONTIC SHALE, INITIAL DENSITY, 1·077.

colloidal properties, whilst the Trinidad sample had a very high colloid content, the Pontic clays being intermediate in colloidity.

The following conclusions on the settling of muds were reached from a study of these and similar curves:—

(I) Settling may be divided into three periods: a preliminary slow period, a main, faster period and a final slow one.

(II) Increase in density causes the periods to become less distinct.

(III) Increase in colloidity causes the periods to become less distinct.

(IV) The higher the density and/or colloidity the greater the initial slow settling period.

(V) The main period settling rate for any given experiment is constant and almost independent of the length of the mud column.

(VI) The time taken for a mud to settle through the main period is roughly proportional to the length of the column.

Mining experts,[6, 7] who encounter similar phenomena in the settling of ore slimes, have explained the three periods as below :—

(I) A short period of slow settling during which the colloidal particles are gradually coagulating to large size flocs. During this short period there may be a slight differential settling of the non-colloidal clay particles originally present.

(II) The flocs settle down at a steady rate, which is almost independent of the length of column, and build up, from the bottom, a sludge.

(III) When the flocs are in contact throughout the length of the mud column, further settling is due to slow compression of the bottom flocs by those above forcing water in the interstitial spaces to the top.

The above readily explains the conclusions reached—for instance, the higher the colloidity or density the longer the time for flocculation, and therefore the longer the initial period : this is excellently illustrated by the mud of Fig. 8, which has no initial period because it was a very dilute suspension and the Kamilal shale has little colloid content.

From the above explanation of the three periods it would be expected that the density at the bottom of the columns would be almost independent of their length, and this was found to be the case.

The density of the bottom 25 cubic centimetres from each of the four columns was determined after 24 hours for runs 1, 2 and 6 and the results were :—

Run.	Original Density.	25 cm.	50 cm.	100 cm.	200 cm.
1	1·077	1·228	1·190	1·210	1·196
2	1·174	—	—	1·256	1·249
6	1·353	1·572	1·602	1·606	1·603

It is this maximum bottom density which is the important factor which will decide whether or not a bit will be jammed at the bottom of the hole if pumping ceases. If a thin stable mud is used, the maximum bottom density, and of course the viscosity, will be low, and cuttings will easily fall back round the bit and clog it, whereas if the mud is not very stable, a thicker sludge will be formed which will hold cuttings suspended more readily : with a mud which gels on standing these considerations scarcely apply, as cuttings will be held in suspension in any case.

The relationship between stability and bottom density was investigated by controlling the settling of a mud by addition of caustic soda and taking the density of the bottom 25 cubic centimetres and the percentage free water appearing after 24 hours, and it was found to be linear. A large-scale settling test was then done, using 44½ feet of 4½-inch drill pipe, with 6 feet of 2½-inch glass tubing cemented into the top. A Pontic mud of density 1·088 was used, and about 100 litres were made up by grinding in a ball mill; the same sample was also settled in 200 centimetres of

1-inch glass tubing. The initial period of slow settling was longer in the case of the drill pipe, and even during the second fast period the 200-centimetre column sank faster, 85·6 centimetres of free water appearing in 24 hours, whereas only 68·5 centimetres had settled in the large-scale test: the 200-centimetre column then entered the third, slow period, whereas the large column continued sinking at the same rate. After 4½ days the bottom density was determined: unfortunately, owing to the draw-off valve choking and then suddenly blowing free, the first litre or so was lost, and the density corresponded to a point about 1 foot up the tube. It was found to be 1·291: the density of the bottom 25 cubic

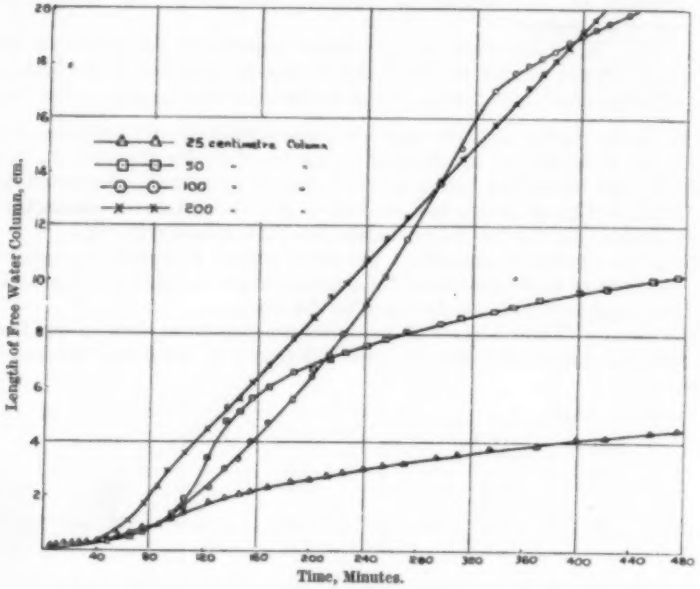

FIG. 10.

SETTLING CURVES FOR A PONTIC CLAY, INITIAL DENSITY, 1·308.

centimetres of the 200-centimetre column was 1·339. Samples from 10, 22 and 32 feet were also taken, and the densities were found to be 1·046, 1·043 and 1·042 respectively, so with this very dilute suspension it is obvious that differential settling had taken place to a large extent, but the interesting point is that over a variation in length of eight times and a difference in diameter of about three times the difference in bottom density was less than 4 per cent., and there would probably have been closer agreement if the first litre from the drill pipe had not been lost. These results seem to show that the increase in bottom density due to settling is almost independent of the length of column, and is therefore not nearly such an important factor as has been supposed.

It will be seen that the most important quality of a drilling mud apart

from its density is its viscous state, and particularly its yield point value, as this will govern—

(I) Its suitability for pumping.

(II) Its ability to hold cuttings suspended and prevent them clogging the bit if pumping ceases.

(III) Its plastering and sealing-off effects.

(IV) Its ability to hold non-colloidal weighting material permanently in suspension.

(V) Its stability: a mud with an appreciable yield point will settle very slowly.

And it is therefore concluded that the only measurement that is necessary on a mud, apart from its density, is of the yield point, either directly by means of a shearometer or by the viscosity at 600 revolutions per minute, and a knowledge of the viscosity/yield point relationship, the stability being but a useful check on the value of the viscous state as given by the shearometer or viscometer.

Furthermore, it is the author's opinion that, in many cases, far too thin a mud is used for drilling. A mud should possess an appreciable yield point and, with the Pontic clay used to obtain Fig. 5, for instance, this means a "viscosity" at 600 revolutions per minute of at least 10 or 12 centipoises. If the mud has a negligible yield point, cuttings will not be held suspended if pumping ceases, and the colloid content will be low, which means bad sealing-off and wall-building properties.

Department of Oil Engineering and Refining,
University of Birmingham.

References.

[1] E. C. Bingham, "Fluidity and Plasticity." New York, 1922.
[2] E. Hatschek, "The Viscosity of Liquids," 1928, p. 207.
[3] Meyer, *J.I.P.T.*, 1934, **20**, 10.
[4] J. F. Dodge, "Petr. Eng. Handbook," 2nd Ed., p. 37.
[5] Strong, *Proc. World Petr. Congr.*, 1933, **1**, 401.
[6] W. A. Deane, *Trans. Am. Electrochem. Soc.*, 1920, **37**, 80.
[7] H. S. Coe and J. H. Clevenger, *Bull. Am. Inst. Min. Eng.*, 1920, p. 597.

THE EXPLOSION OF MIXTURES OF COMBUSTIBLE GASES WITH AIR, BY NUCLEAR DROPS OF WATER AND OTHER NUCLEI AND BY X-RAYS.

PART V. THE EXPERIMENTAL CONDITIONS REQUIRED FOR THE IGNITION OF HYDROGEN–AIR MIXTURES BY NUCLEI.*

By R. O. King, M.A.Sc. (McGill), and George Mole, B.Sc., A.R.C.S., D.I.C.

Introduction.

Characteristics of self-, nuclear and X-ray ignition temperatures of H_2–air mixtures passing through combustion tubes of various materials were described in Parts I–III.[1] The experimental results indicated that self-ignition, when it occurred, was initiated in the layer of gas adjacent to the heated wall of the tube, the temperature of the effect depending on the degree of dilution of that layer with the steam formed by *flameless* combustion on the surface. The provision of a steam-diluted layer tending to remain adjacent to the heated wall and to enclose a central stream of undiluted mixture was favoured by fixing the combustion tube in a vertical position, admitting the gaseous mixture at the lower end and arranging suitable peripheral outlets in the cover of the upper end. The central stream of gas was, in the circumstances, difficult and sometimes impossible to ignite by heating the combustion tube, but ignition and explosion followed the introduction into the gas of nuclear drops of water or dust.

The observed temperatures of self- and nuclear ignition supported the given explanation of the controlling experimental conditions, but further confirmation has been obtained by direct measurement of the steam-forming activities of various combustion tube surfaces and by observations of corresponding ignition temperatures. The more important of these experiments are described in the sections following.

Method of Measurement.

The H_2–air mixture was admitted to the lower end of the combustion tube fixed vertically in an electric furnace and raised to the temperature of the experiment while passing through it. The temperature was taken as indicated by a thermocouple fixed on the vertical axis at the position of maximum temperature and enclosed in a vitreosil sheath. The gaseous mixture leaving the combustion tube passed through a condenser, and

* Air Ministry Official Report, Crown copyright reserved. Received March 27th, 1935.

the water produced was measured and weighed at intervals of about 30 minutes. The arrangement of apparatus is shown by Fig. 1. The steel combustion tubes were oxidized before use to enhance the steam-forming surface activity, and it was possible, therefore, to run an experiment at a temperature higher than that at which an explosion might occur if the surface were clean. The steel headpiece of the tube was, however, fitted with a safety cap free to blow off in the event of an explosion. When ignition temperatures were to be observed, the cap was replaced

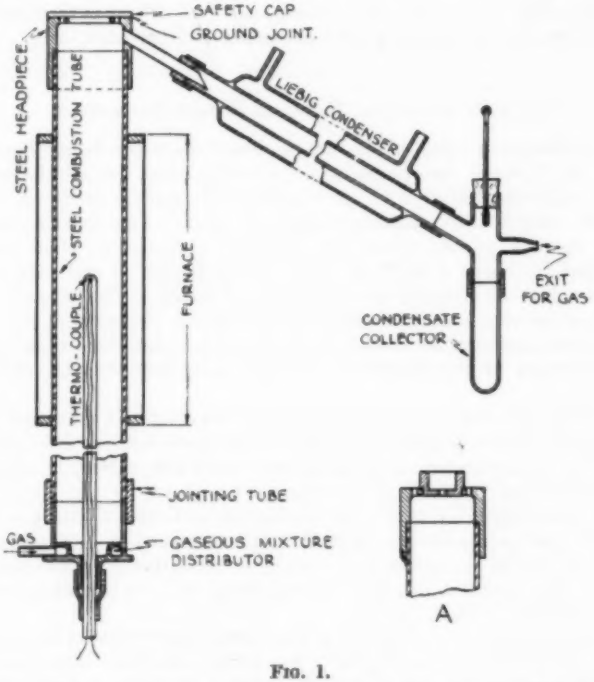

FIG. 1.

ARRANGEMENT OF COMBUSTION TUBE, CONDENSER, AND CONDENSATE COLLECTING DEVICE.

by the bushing illustrated at *A*, Fig. 1. The ring of small holes in the headpiece was thus uncovered to provide a suitable free exit for the gas passing through the combustion tube, and water could be injected through the central hole in the bushing for determinations of nuclear ignition temperatures. The water-collecting device shown by the figure, providing a narrow exit from the condenser, which could not be blocked with water, was designed to prevent atmospheric air from entering the combustion tube via the condenser. The methods of injecting water, measuring rates of gas flow, mixture proportion and temperature were as described in Part I,[1] the temperature of the experiment being taken as

indicated by a thermocouple adjusted along the vertical axis of the tube to the position of maximum effect. Temperatures thus observed are 26°, approximately, lower than the maximum temperature of the tube wall when oxidized steel combustion tubes are used, according to difference measurements to be described in a later part. The hydrogen and air, as supplied directly from high-pressure cylinders, were of corresponding dryness, but both gases were passed over phosphorus pentoxide before entering the combustion tube. A correction to the weight of water collected was therefore required to allow for the water-vapour content of the exit gas, but when using steel combustion tubes, the rate of water formation was so great that the correction was of the order of 3 per cent. only.

Factors affecting Rate of Steam Formation.

The combustion tubes of 1¼-inch internal diameter being fixed in a short (7-in.) furnace, the temperature gradient from the middle is steep, and, for example, about 2 in. in length of the middle part will show a red heat, whilst the remainder appears black. The gaseous mixture flowing upward passes, therefore, through a relatively short reaction zone—that is, about 2 to 3 in. only of the length of the tube surface becomes active to promote the formation of steam. The velocity of the steam-forming reaction, in equilibrium conditions, depends on the factors of catalytic activity, surface temperature and the rate at which the electrolytic gas in the mixture is brought into contact with the active surface.

The factor of catalytic activity has been investigated, but need not be dealt with in detail at present. The overall steam-forming effect is found to vary in a particular combustion tube with the variety, temperature and distribution of the surface oxide, and steam is not formed at a constant rate until, for particular conditions and rate of mixture supply, the oxide attains equilibrium with the H_2 concentration. Determinations of rates of steam formation were made in conditions approaching equilibrium; this state was taken as existing when the rate of steam formation became nearly constant.

The H_2–air mixture is regarded as electrolytic gas * diluted with nitrogen plus H_2 for rich mixtures or plus O_2 for weak mixtures. Steam is formed as the mixture passes over a catalytic surface of excess activity at a rate depending on that at which the electrolytic gas can reach it by diffusion through the diluent. The possible rate of diffusion increases as the mixture density diminishes with increase of H_2 concentration. Thus the increase in percentage rate of electrolytic gas consumed, observed always to correspond with an increase of H_2 concentration, is due in large part to the corresponding diminution of density facilitating diffusion of the electrolytic gas to the active surface. It is important to note that the electrolytic gas in the mixture is also brought into contact with the heated wall to an extent depending on the degree of turbulence in the stream of gaseous mixture flowing through the combustion tube.

* Electrolytic gas is a mixture of H_2 and O_2 in combining proportions.

Measurements of Rates of Steam Formation using Steel Combustion Tubes.

Chromium–nickel steel and nickel steel tubes were used for the experiments. Both tubes were of 1¼ in. internal diameter, cold drawn and descaled before use. The first mentioned was of the 18 per cent. Cr,

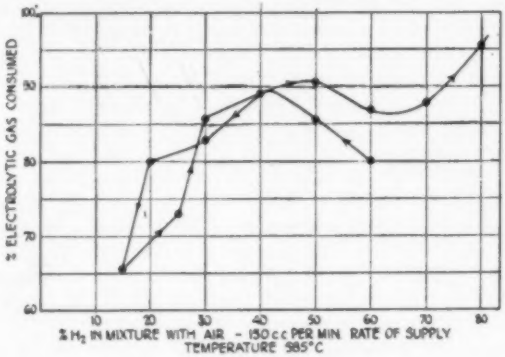

Fig. 2.

Rate of steam formation for H_2 concentrations decreasing from 60% to 15% and then increasing to 80%. Cr–Ni–steel combustion tube.

8 per cent. Ni variety in general use as "Staybrite" steel. The other was of the 3 per cent. nickel steel also in general use. The experiments with both tubes were made at a temperature of 585°, as indicated by the

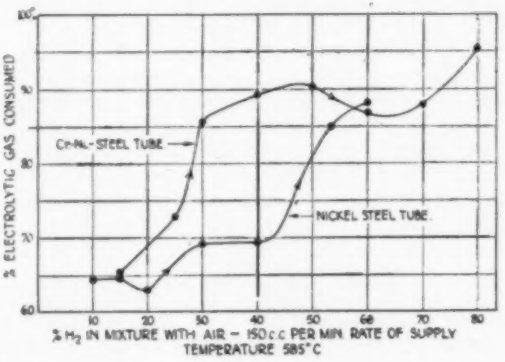

Fig. 3.

Rate of steam formation in similar conditions for the Cr–Ni–steel tube and the Ni–steel tube.

central thermocouple; the maximum temperature of the tubes was therefore 611°, approximately, according to the difference measurements mentioned earlier. The rates of steam formation were measured while

the H_2–air mixture was supplied at the rate of 150 c.c. per minute and at H_2 concentrations varying from 10 to 80 per cent.

The experimental results obtained when using the chromium steel tube are given graphically by Fig. 2, for H_2 concentrations varying from 15 to 80 per cent. It will be seen that 65 per cent., approximately, of the electrolytic gas in the mixture was converted into steam at the lower concentration, and that nearly complete conversion was obtained at the higher concentration. The direction of the change of H_2 concentration during the experiments is shown by the arrows on the graphs. The separation of the graphs, depending on the direction of change, indicates that the activity of the surface oxide varied with that factor or that the equilibrium oxide was not always obtained for every H_2 concentration of the experiments.

The experimental results obtained when using the nickel steel tube are given graphically by Fig. 3; the determination of rate of steam formation beginning with a H_2 concentration of 10 per cent., increased by steps to 60 per cent. The graph for the results obtained for the chromium steel tube in similar conditions is plotted on the figure. Comparing the two graphs, it appears that the respective surface oxides are of approximately equal activity to form steam when the H_2–air mixture is either very weak or very rich in hydrogen, but the activity of the chromium steel tube is from 20 to 28 per cent. greater than that of the nickel steel tube when the H_2 concentration is that required for combining proportions or for somewhat richer mixtures.

The general trend of the graphs of Figs. 2 and 3 supports the view that the percentage consumed of the electrolytic gas available increases with increasing H_2 concentration, owing to the operation of the diffusion factor. The character of the graphs and the effect of changing from chromium to nickel steel show, however, that the surfaces vary in activity according to the nature of the oxides formed on them.

The equilibrium oxide formed on either surface when the H_2 concentration exceeded 50 per cent. was of unexpectedly high activity, and relative values for rates of reaction could not be determined because either oxide converted so nearly all the available electrolytic gas into steam. Further experiments were made, therefore, with the rate of mixture supply increased from 150 to 500 c.c. per minute, but the expectation that the percentage rate of combustion might diminish accordingly was not realized.

Nuclear Drop and Self-ignition Temperatures—Chromium Steel Combustion Tube.

The ignition temperatures given graphically by Fig. 4, Part I, the H_2–air mixture being supplied at the rate of 150 c.c. per minute to a chromium steel tube, were obtained without allowing the surface oxide to reach equilibrium between observations taken over a range of H_2 concentration. It was found to be necessary, in the circumstances, to increase the rate of mixture supply to 200 c.c. per minute, to separate completely the graph for self-ignition from that of nuclear ignition. It was therefore of interest to observe self- and nuclear drop ignition tem-

peratures in the approximate equilibrium conditions of the steam formation determinations described above, the apparatus, as already explained, having been arranged to make this possible. The self- and nuclear drop ignition temperatures observed accordingly are given graphically by Fig. 4. It will be seen that complete separation of the graphs has been obtained, and that values depend to some extent on the direction of

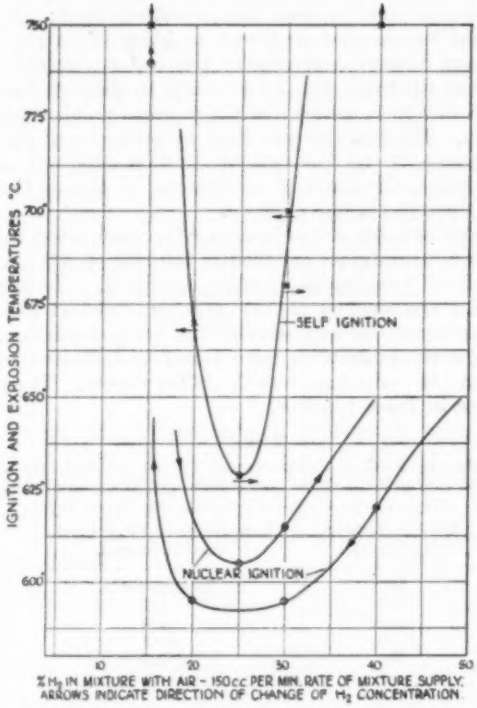

FIG. 4.

NUCLEAR DROP AND SELF-IGNITION TEMPERATURES. Cr–Ni–STEEL COMBUSTION TUBE.

change of H_2 concentration, as would be expected from the fact that the rate of steam formation was found to depend on the same factor.

RATE OF STEAM FORMATION WITH A SILICA COMBUSTION TUBE.

The explosion temperature observed when a H_2–air mixture is heated while passing through a combustion tube of silica or other vitreous material is given frequently as the "ignition temperature." It is of interest, therefore, to determine the corresponding rate of steam formation in conditions similar to those used for the experiments with steel combustion tubes, in view of the fact that with the latter, the temperature of

self-ignition appeared to be governed by the rate of steam formation on the tube surface.

A clear silica tube being inserted as a liner in the steel combustion tube, the sole change in conditions was that the internal diameter of the combustion tube was reduced from 1¼ to 1 in. The special features of the arrangement were: (1) the surface heated to the temperature required for reaction with the gaseous mixture was of silica only; (2) the joint at the hot upper end was steel to steel and remained tight; (3) a gas-tight safety-cap could be provided as shown to blow off on explosion of the mixture, without damage occurring to the water-collecting device; (4) the lower ends of the tubes were cool enough to allow rubber joints to be made in such a way as to ensure that the mixture supplied passed into the silica tube only. The mixture was dried as before by phosphorous pentoxide, and because of the low rate of reaction expected, arrangements were made to collect the water of combustion by passing the gas leaving the condenser through calcium chloride.

Determinations of rates of combustion were made when using a 40 per cent. hydrogen in air mixture supplied at the rate of 200 c.c. per minute, by the method of weighing as already described. The determinations were begun at a temperature of 500° and continued at higher temperatures until interrupted by explosion of the gaseous mixture. The temperatures of the determinations were taken as indicated by a thermocouple fixed on the central axis as described earlier. The experimental results are given in Table I, below.

TABLE I.

Rate of Combustion at Various Temperatures of a 40 per cent. H_2 in Air Mixture passed into a Silica Tube at the Rate of 200 c.c. per Minute.

Temperature as Indicated.	Percentage of Electrolytic Gas Consumed.
500°	inappreciable
550	1·0
570	5·5
580	11·3
587	explosion

It will be observed that the rate of steam formation in the silica tube is small relatively to that measured when the tube was of steel, and that ignition occurred in the silica tube at 587°. When, however, the 40 per cent. hydrogen mixture was passed into the chromium steel tube, nearly 90 per cent. of the electrolytic gas in the mixture was converted into steam by flameless combustion (Fig. 2), and ignition could not be obtained by heating it to any temperature attainable (Fig. 4). The rate of combustion of electrolytic gas was less, at 69 per cent. of the total (Fig. 3) when the mixture was passed into a nickel steel tube and the self-ignition temperature was found to be 650°.

CONCLUSION.

The experimental results confirm the view stated—namely, that self-ignition temperature rises as surface activity increases. The ignition of

the H_2–air mixture cannot therefore arise *on* the surface—that is, the adsorbed layer is converted into steam, but does not ignite in the process. The ignition effect apparently does not occur in the purely gaseous phase or central stream because if steam is formed on the surface at a suitable rate, the central stream cannot be ignited at any temperature attainable by heating the tube; nevertheless a sufficient proportion of electrolytic gas remains in it to ignite and explode if nuclei are provided. The conclusion is that self-ignition, when observed, occurs in the layer of gas adjacent to the hot surface, described conveniently as the boundary layer. This view is supported by the X-ray ignition effect described in Part II, which, as was stated, is in accordance with the prediction by J. J. Thomson that chemical change would be expected to proceed with high velocity in the electrified layer of gas supported by a heated surface.

The experimental method adopted to enclose a body of combustible mixture in a non-reactive envelope applies to H_2–air mixtures especially, but can be employed usefully with other gases and fuel vapours. The experimental results obtained with H_2–air mixtures are of interest in respect of current theories of ignition and explosion, but discussion is postponed until further experiments are described.

Reference.

[1] King and Mole, *J.I.P.T.*, 1934, **20**, 791–820.

PART VI. THE NUCLEAR DROP IGNITION TEMPERATURES OF ETHYLENE–AIR MIXTURES PASSING THROUGH A *SILICA* COMBUSTION TUBE; THE RELATION BETWEEN WALL AND GAS TEMPERATURE AND THE EFFECT ON IGNITION TEMPERATURES OF THE CENTRAL THERMOCOUPLE SHEATH.

By R. O. King, M.A.Sc. (McGill), and George Mole, B.Sc., A.R.C.S., D.I.C.

Introduction.

The characteristics of the effect of nuclear drops of water to ignite and explode ethylene–air mixtures passing through a nickel-steel combustion tube were described in Part IV.[1] The nuclear igniting effect is less easily obtained when the combustion tube is of silica, this material being relatively inactive to form, by reaction with the combustible mixture, a layer of steam tending to protect the mixture from ignition by the heated surface, as described in Part V. The conditions required for nuclear drop ignition when using a silica combustion tube have been determined since the earlier experiments were made, and are of interest concerning the mechanism of ignition, but before describing them it will serve a useful purpose to give the results of a number of experiments that help to answer questions raised about the method of measuring temperature and the effect of the thermocouple sheath on ignition temperature as observed.

The experiments, being made with a gaseous mixture passing through an externally heated combustion tube supported vertically, the tem-

perature of the mixture has been taken as a matter of convenience, as indicated by a thermocouple fixed on the vertical axis at the position of maximum temperature and protected by a vitreosil sheath. The temperature of the gaseous mixture, thus measured, is necessarily lower than that of the tube wall, and the placing of the thermocouple sheath directly in line with the pump nozzle introduces a possible igniting effect due to part of the injected water striking the sheath and splashing from it. Moreover, the possibility of ignition being initiated by the surface of the vitreosil sheath requires investigation, especially when using a gas such as ethylene, which cannot, because of the relatively high density, reach the heated wall by diffusion as readily as hydrogen.

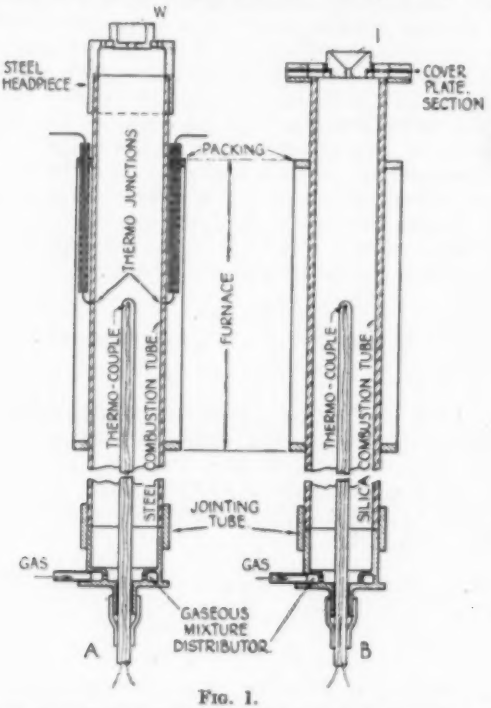

FIG. 1.

COMBUSTION TUBES WITH INTERCHANGEABLE UPPER END FITTINGS, W FOR WATER INJECTION, I FOR INCOMBUSTIBLE POWDER.

A. Nickel-Steel Tube fitted with Wall Thermo-Junction. B. Silica Tube.

THE RELATION BETWEEN THE MAXIMUM TEMPERATURE OF THE COMBUSTION TUBE AND THAT INDICATED BY THE CENTRALLY FIXED THERMOCOUPLE.

The wide range of rate of flow of the gaseous mixture, corresponding with a rate of mixture supply varying from 50 to 500 c.c. per minute,

the unknown emissivity of the heated surface of the combustion tube and the relatively short length of furnace, are factors affecting the relation between the temperature of the surface and that of the gaseous mixture as indicated by the thermocouple fixed on the vertical axis of the tube. The temperature of the tube surface is always the higher, and can be taken as that of self-ignition of H_2–air mixtures, because for these ignition could be seen, through a window in the top cover of the tube, to start adjacent to the surface, whatever the material of the tube. The self-ignition of ethylene–air mixtures began similarly in particular cases only, otherwise it started in the body of the gaseous mixture, and the temperature would then be expected to lie between that of the wall surface and that indicated by the central thermocouple.

The arrangement of apparatus used to relate the tube temperature to that indicated by the central thermocouple is shown at *A*, Fig. 1. Iron and constantan wires, the elements of the thermocouple, were welded into the nickel-steel combustion tube at diametrically opposite points in the hottest part of the surface. The thermocouple within the vitreosil sheath remained as before. The two thermocouples were of specimens of iron and constantan from the same batches (Cambridge Instrument Company, Batch No. 738). The cold junctions were situated close together. A two-way switch was used to connect either thermocouple to a single calibrated indicator. The temperatures indicated were observed in steady conditions always, over the temperature range 500–770°, and while nitrogen was supplied to the combustion tube at rates varying from 25 to 400 c.c. per minute. Experimental results are given in Table I for a clean and an oxide-coated tube surface.

TABLE I.

Excess of Maximum Temperature of Clean and Oxidized Steel Combustion Tubes over Temperature Indicated by Central Thermocouple, with N_2 Passing Through at Various Rates.

Max. Temp. Tube Wall, ° C.	Excess of Wall Temperature over Central Temperature for Rates of N_2 Supply of 25 c.c. to 400 c.c. per Minute.									
	25 c.c.		50 c.c.		100 c.c.		200 c.c.		400 c.c.	
	Clean.	Oxi-dized.	Clean.	Oxi-dized.	Clean.	Oxi-dized.	Clean.	Oxi-dized.	Clean.	Oxi-dized.
500	20	25	20	23	19	21	17	20	16	19
530	22	28	22	27	21	25	20	23	19	22
590	23	28	23	28	22	27	21	25	20	24
650	24	30	24	30	24	29	23	28	22	28
680	25	30	25	30	25	29	24	28	24	27
710	26	30	25	30	25	29	25	29	24	28
770	27	33	27	31	28	31	28	30	28	30

It will be seen by reference to the table that the wall temperatures are from 16° to 30° higher than the temperatures indicated by the central thermocouple, and that the difference is always the greater by from 2° to 5° when the tube surface is coated with oxide.

The sources of temperature difference fall into the following classes :—

(1) A possible cooling effect by the gas on the central thermocouple, at the higher rates of flow.

(2) The reception by the central thermocouple sheath of radiation from parts of the heated wall at temperatures lower than the maximum.

(3) A difference due to the sub-unity values of the emissivity, for the surfaces of thermocouple sheath and tube.

(4) A difference due to heat liberated by surface combustion when a combustible mixture is passed through the tube.

Any temperature difference due to (1) appears to be negligible, because it will be seen, by reference to Table I, that the measured difference falls instead of rises as the rate of gas flow is increased, until the temperature exceeds 700°. The observed temperature difference appears to be due mainly to (2). Thus the wall thermocouple measures the maximum temperature of the tube, whereas the temperature of the couple within the central sheath is due to radiation from a considerable length of the combustion tube wall, on which there is a steep temperature gradient from the middle towards the ends; a mean temperature is therefore indicated.

The increase of temperature difference observed on changing from a clean to an oxide-coated surface is attributed to (3). Thus, the emissivity of an iron surface was found to be 0·3 approx. by Thwing,[2] and that of an iron oxide surface to be 0·85 by Burgess and Foote.[3] The conclusion is that the maximum temperature of the gas in the central part of the tube has some value intermediate between that of the wall and that indicated by the central thermocouple.

Observations of ignition temperatures, taken nearly simultaneously by the wall and central thermocouples, showed that no appreciable difference could be attributed to (4) when using a combustible mixture of 9 per cent. ethylene concentration. An appreciable temperature difference might arise, however, from the heat of combustion when using, for example, a 40 per cent. H_2 in air mixture and a steel tube, because then nearly all of the electrolytic gas in a mixture supplied at any rate up to 500 c.c. per minute would be burnt to steam on the surface of the tube.

Nuclear and Self-ignition Temperatures of Ethylene–Air Mixtures Observed with and without the Central Thermocouple.

The relation between the temperature of the tube wall and that indicated by the centrally fixed thermocouple having been obtained as described, it is obvious that nuclear and self-ignition temperatures such as would be indicated by a centrally fixed thermocouple can be obtained by observations of wall temperature alone, the central thermocouple and vitreosil sheath being withdrawn. Nuclear and self-ignition temperatures observed accordingly are given graphically by Fig. 2, for a particular ethylene–air mixture supplied to the nickel-steel combustion tube at rates varying from 100 to 500 c.c. per minute. The lower pair of graphs shows nuclear and self-ignition temperatures as indicated in the usual way by the thermocouple enclosed in the centrally fixed sheath. The upper pair of graphs shows corresponding ignition temperatures as indicated by the thermojunctions in the tube wall, the central thermocouple and sheath being removed. It will be observed that the temperature differences between

the graphs agree closely with the differences given in Table I for corresponding temperatures and rates of gas supply.

The experiments confirm that the striking of part of the injected water on the thermocouple sheath is without effect on the nuclear ignition temperatures of ethylene–air mixtures. A similar conclusion in respect of H_2–air mixtures was reached as a result of observations of nuclear ignition temperatures made when the thermocouple was enclosed in a small vitreosil tube fixed close to the wall of the combustion tube, and thus not in line with the direction of water injection (Part I).

The experiments indicate also that the surface of the thermocouple sheath is without effect on the self-ignition temperatures of ethylene–air mixtures. Self-ignition, if arising solely from the action of a heated surface, would be expected to begin in the layer of gas adjacent to the hottest part of the combustion tube wall, rather than in the cooler layer

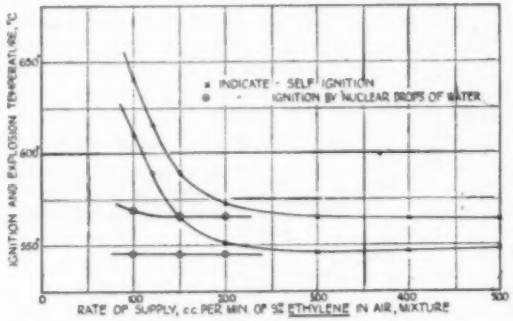

FIG. 2.

Lower Pair of Graphs. SELF- AND NUCLEAR DROP IGNITION TEMPERATURES OF AN ETHYLENE–AIR MIXTURE PASSING THROUGH A Ni–STEEL COMBUSTION TUBE AS INDICATED BY A CENTRALLY FIXED THERMO-COUPLE IN SHEATH.

Upper Pair of Graphs. SIMILAR IGNITION TEMPERATURES AS INDICATED BY WALL THERMO-JUNCTIONS, THE CENTRAL SHEATH AND THERMO-COUPLE BEING WITHDRAWN.

adjacent to the thermocouple sheath. The surface of the sheath as compared with the wall surface may therefore be neglected as a factor to start ignition, in the conditions of the experiments. Ignition in ethylene–air may, however, begin in the gaseous mixture apart from a fixed surface, as mentioned earlier, and the hypothesis has been advanced that it is a nuclear effect following the attainment of a suitable concentration of fog particles, described as oxidation nuclei. The maximum temperature of the oxidation nuclei formed in the gas would be higher than that of the thermocouple sheath, according to the experiments described above, and ignition would therefore be expected in the gas adjacent to the nuclei rather than in the layer adjacent to the sheath.

The Self-ignition Temperatures of Ethylene–Air Mixtures as Affected by the Material of the Combustion Tube.

It was observed in earlier experiments, made in association with the late Professor Callendar and others,[4] that when hydrocarbon vapours or

gases, mixed with air, were passed through a glass combustion tube and the temperature of part of the tube was raised gradually, the first sign of combustion was the deposition of dew (condensed steam) on the cool part of the tube. The effect was most pronounced for the paraffin hydrocarbons. The steam is a product of surface combustion proceeding to the *final* stage prior to and at a lower temperature than the gaseous phase oxidation yielding partial products initially. The steam arises necessarily in the conditions from the combustion of hydrogen on the heated surface. The hydrogen may be regarded as becoming available from the decomposition of the hydrocarbon molecule on the surface of the combustion tube or, at higher temperatures, from molecular decomposition (cracking)

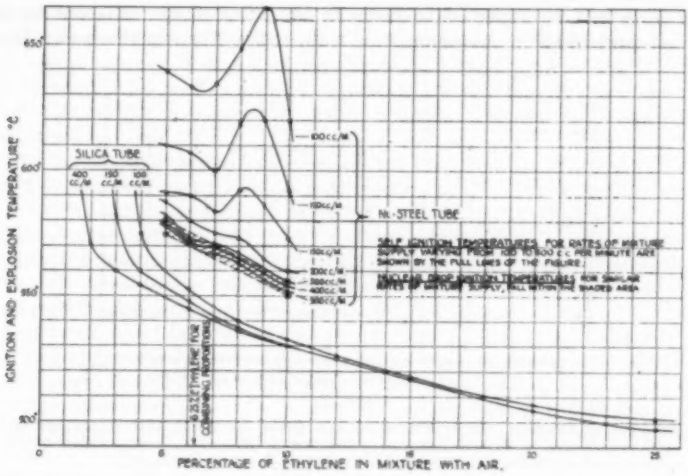

FIG. 3.

THE EFFECT OF SILICA AND OXIDIZED Ni–STEEL SURFACES ON THE IGNITION OF ETHYLENE–AIR MIXTURES.

in the vapour phase. The hydrogen becoming available on passing an ethylene–air mixture through a combustion tube at a given rate would undergo combustion to steam at a rate depending on the nature of the tube surface. The rate would be expected to be a minimum on a silica surface, and has been shown to be many times greater on a steel or iron surface in a state of oxidation (Part V). The layer of steam formed on the surface as a product of combustion dilutes the adjacent layer of mixture and raises the ignition temperature. The gaseous mixture passing through the tube tends to be protected accordingly from ignition by the hot surface. It would be expected, therefore, that the self-ignition temperature of an ethylene–air mixture passing through a steel combustion tube would be higher than would be observed on passing the mixture through one of silica, temperatures being taken as indicated by a thermocouple on the axis of the combustion tube.

The results of experiments made to confirm the expectation by showing

the effect of combustion tube surface activity on the self-ignition temperatures of ethylene–air mixtures are given graphically by Fig. 3. The upper set of graphs showing self- and nuclear ignition temperatures of the mixture supplied to a nickel-steel combustion tube at rates varying from 100 to 500 c.c. per minute is reproduced from Fig. 3 of Part IV. The lower set of graphs shows the corresponding ignition temperatures observed when the combustion tube was of clear silica of the same diameter (1¼ in.) as the steel tube, and similarly supported vertically in the 7-in. electric furnace. It will be seen that not only does the temperature of self-ignition diminish on changing from the active steel surface to the relatively inactive silica surface, but the range of inflammability increases to a remarkable extent. It was difficult, and generally impossible, to ignite and explode a mixture containing less than 6 per cent. of ethylene when using the steel combustion tube, but when the tube was of silica, the effect could be obtained with an ethylene concentration of 2 per cent. only. The upper limit of inflammability of ethylene–air mixtures is known to be of an indefinite character. The mixture burns when ignited, but the rate of flame propagation is too slow to give an explosion effect. The "explosions" in the steel tube following ignition remained just audible on attaining an ethylene concentration of 10 per cent., but those in the silica tube were of similar intensity when the concentration reached 25 per cent.

Ethylene–air mixtures passing through a silica tube were ignited by drops of water in the course of the preliminary experiments mentioned in the introduction to Part I. The conditions required for the effect were, however, not understood, and later attempts to repeat it were unsuccessful. Experiments made still later, with hydrogen–air mixtures, led to an understanding of the conditions required, by showing that nuclear ignition is obtainable generally when a layer of steam protects the mixture from prior ignition by the heated tube surface. The conditions were obtained at once on using a steel combustion tube, and experiments made accordingly are described in Part IV. They support the view that ignition from the surface being prevented by steam dilution of the adjacent layer of gaseous mixture, the effect is then obtained on the surface of nuclei in the gaseous stream, in suitable conditions of temperature and ethylene concentration. Ignition in the gaseous mixture would be expected, therefore, when oxidation nuclei attain a suitable concentration, but the effect can be induced previously by providing nuclear centres in the form of fine particles of water or dust; thus referring to Fig. 3, upper part, nuclear drop ignition temperatures fall in the narrow band between the broken lines and the temperatures of self-ignition tend to fall to the same values as the concentration of oxidation nuclei increases with increase of ethylene concentration and rate of supply.

When a silica, instead of a steel, combustion tube is used for experiments, it would be expected, therefore, that nuclear drop ignition would be obtainable only in conditions such that the relatively small rate of steam formation on a silica surface would suffice to protect from ignition a mixture not liable to form a high concentration of oxidation nuclei. The conditions are satisfied for ethylene–air by supplying the mixture to the combustion tube at relatively small rates and ethylene concentrations. The results of experiments made accordingly to determine nuclear

drop and self-ignition temperatures are given graphically by Fig. 4. It will be seen by reference to the figure that the self-ignition temperature always approaches a limiting minimum value for any particular ethylene concentration, as the rate of mixture supply is increased. Nuclear drop ignition is obtained at the lower rates of flow, for concentrations of 3 to 8 per cent. of ethylene. The nuclear ignition graphs differ from those obtained with a steel combustion tube, by running into the self-ignition

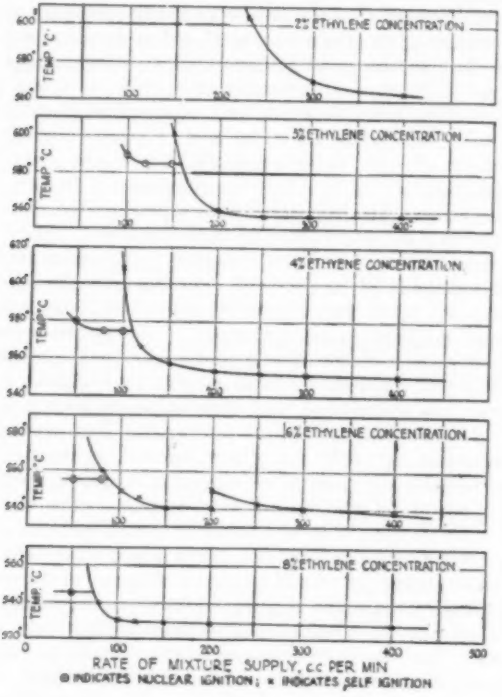
2% ETHYLENE CONCENTRATION
3% ETHYLENE CONCENTRATION
4% ETHYENE CONCENTRATION
6% ETHYLENE CONCENTRATION
8% ETHYLENE CONCENTRATION
TEMP °C
RATE OF MIXTURE SUPPLY, c.c PER MIN
⊙ INDICATES NUCLEAR IGNITION; × INDICATES SELF IGNITION

FIG. 4.

EFFECT OF *ETHYLENE* CONCENTRATION IN MIXTURE WITH AIR AND RATE OF MIXTURE SUPPLY ON SELF- AND NUCLEAR DROP IGNITION TEMPERATURES. *Silica Combustion Tubes.*

graphs at temperatures above the limiting minimum value, instead of at the limiting value. The difference in character appears to be due to the dissimilar origin of the ignition; the effect was seen to begin adjacent to the *surface* of the relatively inactive silica tube when the concentration of oxidation nuclei in the body of the gas was insufficient to start ignition there. That is, the relative amount of surface combustion being increased by lowering the rate of mixture supply, it becomes possible thus to delay ignition of the gas adjacent to the heated surface, and the temperature of the body of the gas can be raised sufficiently to obtain nuclear drop

ignition, provided also that ethylene concentration is relatively small and the formation of oxidation nuclei delayed accordingly.

When a steel combustion tube is used, ignition cannot be seen to start in the layer of gas adjacent to the surface, presumably because the effect is not propagated from the wall, owing to the dilution of the surface layer of gas with the products of the flameless combustion proceeding on the oxidized steel surface at high velocity. Ignition then occurs as self-ignition in the gaseous phase when the temperature, concentration of ethylene and rate of mixture supply combine to provide the requisite concentration of nuclei, or when that factor is provided from an external source as fine particles of water or dust.

Acknowledgment is made to the Cambridge Instrument Company for assistance with the preparation of the wall thermo-junctions shown by Fig. 1 A.

References.

[1] King and Mole, *J.I.P.T.*, 1934, **20**, 791–820.
[2] Thwing, *Phys. Rev.*, 1908, **26**, 190.
[3] Burgess and Foote, *Bur. Stand. Bull.*, **1**, 1914.
[4] Callendar, King, Mardles, Stern and Fowler, Aero. Res. Ctte. R. & M. No. 1062; also *Engineering*, Feb. 4th *et seq.*, 1927.

PART VII. THE EFFECT OF A VARIETY OF NUCLEI, MAINLY MINERAL DUSTS, TO IGNITE AND EXPLODE A MIXTURE OF HYDROGEN AND AIR; THE EXCEPTIONAL EFFICACY OF Ni_2O_3 DUST TO IGNITE MIXTURES OF AIR WITH HYDROGEN, ETHYLENE OR METHANE.

By R. O. King, M.A.Sc. (McGill), and George Mole, B.Sc., A.R.C.S., D.I.C.

Introduction.

Experiments described in Parts I to VI having shown that the explosion of certain gaseous combustible mixtures is promoted by the presence in them of incombustible nuclei differing in character so widely as water particles and stone dust, it would be expected that nuclei of any sort would be effective centres of ignition. Experiments have been made accordingly, selecting as nuclei powdered compounds of the metals iron, lead, zinc and chromium. All the nuclei were found to be effective, in various degrees, to explode a mixture of H_2–air. The variations were such as might be attributed to variations in sizes of the particles, omitting from consideration the exceptional igniting effect found to be possessed by Ni_2O_3.

Method of Experiment.

The arrangement of a combustion tube in a vertical furnace 7 in. long, and the methods of measuring rates of supply of the combustible gases and air, were as described in earlier parts. Ignition and explosion temperatures were taken as indicated by the thermocouple fixed on the vertical axis of the combustion tube at the position of maximum temperature and

protected by a vitreosil sheath. A chromium–nickel-steel combustion tube was used in the first instance, and a clear silica tube for the later experiments. The combustion tubes were 1½ in. internal diameter. The device for dropping the powdered substances into the gaseous mixture was better adapted for the purpose than the glass funnel used in the first experiments with stone dust (Part IV), which when tapped allowed an indeterminate quantity of dust to fall in an accidental direction into the gas. Thus a small conical dipper was used for picking up the dust to ensure that the volume dropped into the gas was always the same. The dipper, when filled level with the top edge, held 5 milligrams of stone dust, and when dumped into the funnel-shaped metal bushing shown at *I*, Fig. 1, Part VI, the contents tended to fall through the central core of the gaseous mixture. The figure mentioned illustrates other details of the apparatus, especially the design of ventilated top end fittings with the interchangeable bushings *I* for incombustible dust and *W* to take the injection nozzle for experiments with drops of water.

The Nuclear Ignition Temperatures of a Hydrogen–Air Mixture, for a Variety of Incombustible Dusts.

It has been explained in previous parts that nuclear ignition is obtained most readily when a steel combustion tube is used, and the gaseous mixture passing through it protected consequently from the igniting effect of the heated wall, by the layer of steam formed thereon. A further advantage is gained in experiments intended to demonstrate nuclear ignition, by using H_2–air as the combustible mixture, because it oxidizes to steam only, on the surface; and secondly, ignition does not begin in the mixture itself unless nuclei are introduced.*

A chromium–nickel-steel combustion tube was prepared for the experiments by suitably oxidizing the interior surface. The hydrogen–air mixture contained H_2 in the proportion of 40 per cent., and was selected because, when passed through the prepared combustion tube, self- and nuclear drop ignition temperatures could both be obtained on the scale of the temperature indicator over a wide range of rate of mixture supply. The ignition temperatures determined accordingly are given graphically by Fig. 1, and serve as a basis of comparison for the nuclear ignition temperatures observed when various incombustible dusts were dropped into the gaseous mixture. It will be understood, from experiments described in earlier parts, that the maintenance of self- and nuclear drop ignition temperatures at steady values depends on the steam-forming activity of the combustion tube surface remaining nearly constant. The use of fine particles of water as nuclei does not foul the surface, and the oxides of iron, chromium, lead or nickel are not objectionable, because when blown on to the surface by an explosion they soon become of somewhat similar catalytic activity. The other substances, such as stone dust, sulphates, etc., tend to poison the surface, and cleaning and re-establishment are necessary after a few explosions have occurred. Therefore after establishing the basis of comparison by using nuclear drops of water as the

* Experiments described in previous Parts support this statement, but it is not in agreement with the opinions of some authorities.

igniting agent, nuclear ignition temperatures were determined using the other substances in the order—iron, nickel, chromium oxides, zinc oxide, lead sulphate, lead sulphide, stone dust. Determinations were made at three rates of mixture supply for the substances having little deleterious effect on the active surface and at one rate for the others. The nuclear ignition temperatures observed when Fe_2O_3, Fe_3O_4 and Ni_2O_3 were dropped into the H_2–air mixture are given by Fig. 1 for rates of mixture supply

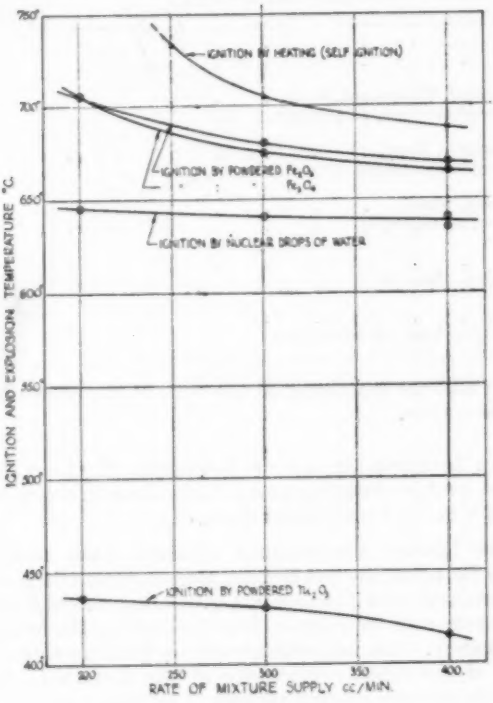

FIG. 1.

IGNITION OF A HYDROGEN–AIR MIXTURE (40% H_2 CONCENTRATION) PASSING THROUGH A Cr–Ni–STEEL COMBUSTION TUBE, BY NUCLEI OF WATER AND OF OXIDES OF IRON AND NICKEL.

varying from 200 to 400 c.c. per minute. It will be seen on reference to the figure that the two oxides of iron are less effective to ignite the mixture than drops of water, but that the nuclear ignition temperature observed when using Ni_2O_3 is more than 200° less than that obtained for nuclear drops of water. The nuclear ignition temperatures observed for all of the substances are given in Table I, in order of magnitude.

The substances of Table I were used as received, and the descriptions are as given by the suppliers. The stone dust was the refractory material of Part III, and was reputed to be powdered alumina mainly. The igniting

effect of the stone dust was found to be greater than that of nuclear drops of water in the experiments described in Part III, but these were made

TABLE I.

The Igniting Effect of a Variety of Incombustible Nuclei on a H_2–Air Mixture, H_2 Concentration 40 per cent., Supplied to a Chromium–Nickel-Steel Combustion Tube at the Rate of 300 c.c. per Minute; Temperature of Ignition by Heating, 705°.

Nature of Substance used as Nuclei.	Nuclear Ignition Temperature, ° C.
Zinc oxide	690
Lead sulphate	685
Iron oxide, calcined, 99 per cent. Fe_2O_3	680
Iron oxide, precipitated red, 85 per cent. Fe_2O_3	680
Iron oxide, magnetic, Fe_3O_4	675
Iron oxide, precipitated brown, 80 per cent. Fe_2O_3	660
Nickel oxide, grey, Ni_2O_3	655
Chromium oxide, green, Cr_2O_3	650
Lead sulphide	645
Stone dust, mainly alumina	645
Water as drops	640
Nickel oxide, Ni_2O_3, iron and cobalt free	430

with a H_2–air mixture containing 50 per cent. of H_2, passed into a nickel steel combustion tube.

THE NUCLEAR IGNITING EFFECT OF POWDERED Ni_2O_3, IN RESPECT OF MIXTURES OF AIR WITH HYDROGEN, ETHYLENE OR METHANE, PASSING THROUGH A SILICA COMBUSTION TUBE.

The nuclear ignition temperatures obtained when using powdered Ni_2O_3 were so far below the self-ignition temperatures of H_2–air mixtures, however determined, that the precaution of using an oxidized steel tube to obtain protection of the mixture from ignition by the heated wall was no longer necessary. The experiments were continued using a silica tube, and because of the relative inactivity of the surface to form steam, the combustible mixture passing through it exhibited the minimum self-ignition temperature and the maximum range of inflammability (Part V). The experimental results for the three gaseous combustible mixtures were as follows:—

(a) *Hydrogen–Air.* The mixture was supplied to the silica combustion tube at the rate of 400 c.c. per minute, and self- and nuclear ignition temperatures were obtained over a wide range of H_2 concentration. The experimental results are given graphically by Fig. 2. It will be observed that the minimum self-ignition temperature, in the conditions of the experiment, is 566°, and that the similar nuclear ignition temperature is 395°. The activity of the heated silica surface to form steam has been shown (Part V) to be inappreciable at temperatures below 500°. Therefore a nuclear ignition temperature observed at 395° is unaffected by reactions occurring on the heated wall. The igniting effect of the Ni_2O_3

might be attributed to pyrophoric nickel produced by the reducing action of the hydrogen, but the occurrence of the minimum nuclear ignition temperature in a mixture of combining proportions instead of in one containing excess H_2 does not support this view.

(b) *Ethylene–Air Mixtures.* Self-ignition temperatures were determined for rates of mixture supply of 50 c.c., 100 c.c. and 400 c.c. per minute, and for concentrations of ethylene in the mixture with air, extending

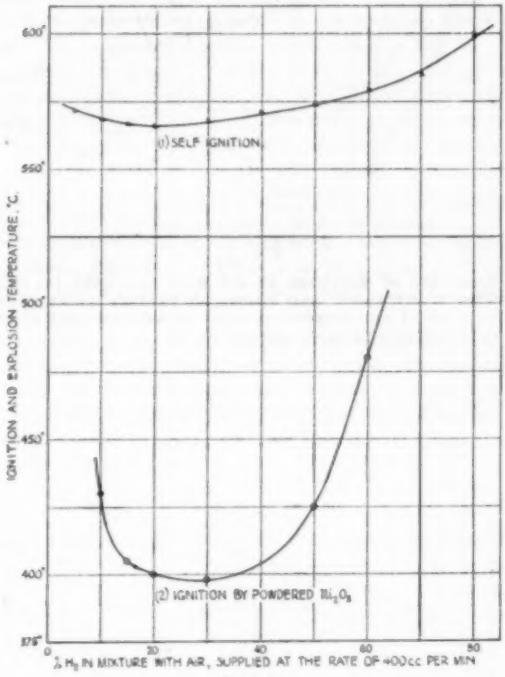

FIG. 2.

IGNITION TEMPERATURES OF HYDROGEN–AIR MIXTURES PASSING THROUGH A SILICA COMBUSTION TUBE.

(1) Ignition by Heating (Self-Ignition).
(2) ,, Powdered Nickel Oxide (Ni_2O_3).

from 2 to 20 per cent. The observations are given graphically by Fig. 3, and may be compared with the nuclear ignition temperatures observed on dropping powdered Ni_2O_3 into the mixture and given on the same figure. The igniting effect of nuclear drops of water, obtainable over a limited range of ethylene concentration for relatively small rates of mixture supply only, is shown on the figure by the broken line graph, for the sake of comparison with the nuclear igniting effect of the powdered nickel oxide. It will be seen at once that the Ni_2O_3 is of relatively less igniting effect on the ethylene–air mixture than on the H_2–air mixture, and that

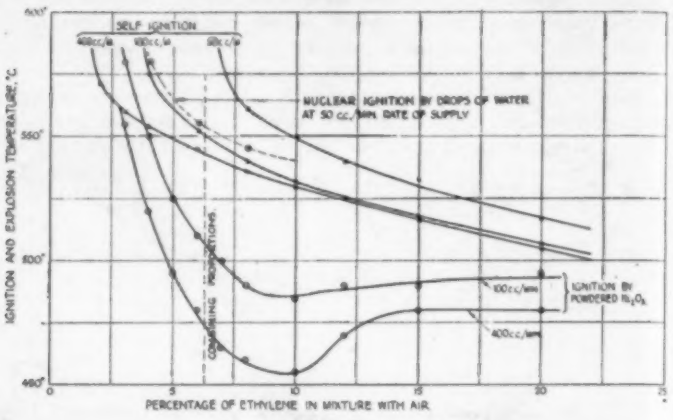
SELF IGNITION
NUCLEAR IGNITION BY DROPS OF WATER AT 50 cc./MIN. RATE OF SUPPLY
COMBINING PROPORTIONS
100 c.c./MIN.
400 c.c./MIN.
IGNITION BY POWDERED Ni_2O_3
IGNITION AND EXPLOSION TEMPERATURE, °C.
PERCENTAGE OF ETHYLENE IN MIXTURE WITH AIR

FIG. 3.

IGNITION TEMPERATURES OF MIXTURES OF AIR WITH ETHYLENE IN CONCENTRATIONS EXTENDING TO 20 PER CENT., AND PASSED AT VARIOUS RATES THROUGH A SILICA COMBUSTION TUBE. *Upper Graphs:* IGNITION BY HEATING (SELF-IGNITION). *Lower Graphs:* IGNITION BY POWDERED NICKEL OXIDE.

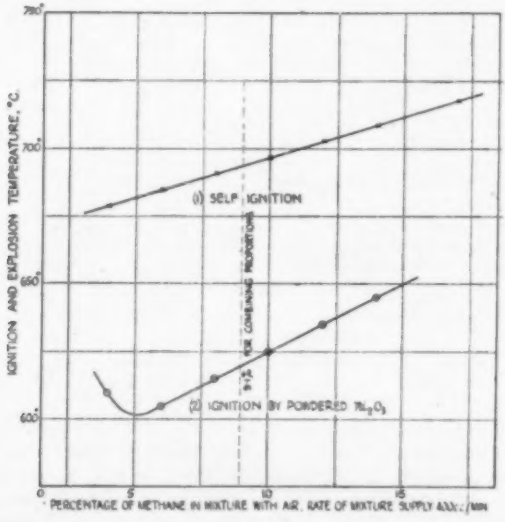
(1) SELF IGNITION
(2) IGNITION BY POWDERED Ni_2O_3
FOR COMBINING PROPORTIONS
9·5%
IGNITION AND EXPLOSION TEMPERATURE, °C.
PERCENTAGE OF METHANE IN MIXTURE WITH AIR. RATE OF MIXTURE SUPPLY 400 c.c./MIN.

FIG. 4.

IGNITION TEMPERATURES OF *METHANE*–AIR MIXTURES PASSING THROUGH A SILICA COMBUSTION TUBE.

(1) Ignition by Heating (Self-Ignition).
(2) ,, Powdered Nickel Oxide (Ni_2O_3).

the maximum igniting effect occurs when the concentration of ethylene is about 50 per cent. in excess of that required for combining proportions.

(c) *Methane–Air.* The causes leading to the ignition and explosion of methane–air mixtures are of especial interest in respect of safety in coal mines. It is regretted, therefore, that laboratory facilities for the experimental investigation of the effect of incombustible nuclei and heated surfaces on the temperature of ignition and range of inflammability of these mixtures ceased to be available in the early stages of the work. Experiments were, however, completed on the igniting effect of powdered nickel oxide. The results are given graphically in Fig. 4. The nuclear ignition temperature is about 75° lower than that of self-ignition, and the minimum nuclear ignition temperature is obtained when the concentration of methane in the mixture is 5·5 per cent.—that is, 50 per cent. less, approximately, than the concentration required for combining proportions. The lower limit of inflammability, so far as the determinations were carried, was 4 per cent. methane, either for self-ignition from the silica surface or for nuclear ignition. The accepted lower limit is 5·6 per cent. This limit is obtained by experimental methods based on starting ignition by a flame, electrical or otherwise, in a small part of a relatively large volume of gaseous mixture. The igniting effects of heated surfaces are neglected in the conditions.

The graphs of Fig. 4, showing the lowering of the ignition temperature of methane–air mixtures by powdered nickel oxide, are remarkably similar in form to those obtained by Lewis and Kreutz [1] for the lowering of the ignition temperature of similar mixtures by electrification of nitrogen prior to mixing it with oxygen and methane in the proportions required to form methane–air mixtures.

Reference.

[1] B. Lewis and C. B. Kreutz. *Jour. Chem. Phys.*, 1933, **1**, 89.

A WIDE RANGE BOILING-POINT CONVERSION CHART FOR HYDROCARBONS AND PETROLEUM PRODUCTS.*

By E. S. L. Beale and P. Docksey (Associate Member).

SYNOPSIS.

The experimental determination of vapour pressures of petroleum distillates and of *n*-dodecane down to low pressures and up to high temperatures is described.

From this and other published data a reliable boiling-point conversion chart is constructed which covers the whole range of vacuum distillation met with in the analysis of petroleum products.

The precautions taken to ensure reliability of the results, particularly at the highest temperatures, are given in some detail, to show that the data can be extrapolated with confidence in the region where accurate experiments are impossible.

Introduction.

There is a definite need for a reliable chart for converting the observed boiling points in vacuum distillations to a common basis. Vacuum distillations are carried out at a variety of pressures (from 0·01 to 15 mm. of mercury) to suit the particular circumstances, and for the analyses to be compared it is necessary to convert to a common pressure. This is usually taken to be 760 mm. of mercury, so that vacuum distillations can be compared with those at atmospheric pressure.

Although it is not essential for the boiling point at 760 mm. of high-boiling fractions (such as of lubricating oil) to be very exact, since boiling points of 500–600° C. are not attainable in practice, it is very necessary that boiling points at the various pressures used in practice should give the same converted temperatures, which is the same thing as saying that over the practical range the boiling points must interconvert accurately.

The vapour pressures of petroleum products have formed the subject of several papers in the literature, but it is noticeable that the amount of experimental work is small, and has mostly been confined to materials of comparatively low boiling point.

The experimental work described in this paper formed part of a general investigation into the Pressure-Volume–Temperature relations of pure hydrocarbons, of mixtures, and of petroleum products up to the critical point, but in the present paper we are mainly concerned with pressures of one atmosphere and below.

The work was arranged to extend the range already covered by the data on pure hydrocarbons. These data form an excellent basis for a vapour pressure and a boiling-point conversion chart, but when critically examined they were found to be seriously limited, particularly when materials of high boiling point are under consideration. For instance, *n*-octane

* Paper received March 27th, 1935.

(b. pt. 125·8° C.) is the highest paraffin the vapour-pressure line of which is known over a wide range. Figures are available for paraffins up to *n*-nonadecane (b. pt. 330° C.) over the range 11–760 mm., and for paraffins up to hexatriacontane at low pressures only.

If the boiling-point chart is to be based on a standard pressure of 760 mm., which is in many ways desirable, it is essential that the boiling point of the samples at 760 mm. should be accurately measurable. Also the samples should be of narrow boiling range, so that their vapour-pressure curves will be of the same slope as those of materials at the column head during the course of a distillation. In addition to such samples, it is desirable to have some the boiling point of which at 760 mm. is above the temperature limit imposed by cracking, and to determine their vapour pressure over the greatest practicable temperature range, so as to assist in the extrapolation which is unavoidable if the standard reference pressure is to be 760 mm.

For these experiments a series of cuts of narrow boiling range was made from Iranian crude oil and from unrefined and refined lubricating oils from the same source, and the vapour pressure lines of selected cuts were determined over a pressure range of 760 mm. to roughly 0·1 mm. of mercury.

Methods of Plotting Vapour-Pressure Data.

There are two general methods of correlating vapour-pressure and boiling-point data. The first is to plot the vapour pressure against temperature, choosing some function of these two variables which will give approximately straight lines for each substance, and which will cover a wide range on one chart.

Ashworth,[1] Cox,[2] and Maxwell,[3] for instance, have used this method, using functions which give as nearly as possible straight lines for pure hydrocarbons, the data for which come to a large extent from the work of Young,[4] and of Krafft.[5]

A simpler relationship is that used first by Wilson and Bahlke [6] for plotting vapour-pressure lines of petroleum products. Log P is plotted against 1/T° abs., and using these scales, lines are obtained which are only slightly curved, and which may be extrapolated with confidence over a short range. These scales are simpler than those used by the authors mentioned above, and have a further advantage in that petroleum mixtures of wide boiling range give vapour-pressure lines which are very nearly straight. The experimental results described in this paper were plotted in this way, and Fig. 3 shows a typical vapour-pressure curve.

The second method is to plot the boiling point at any pressure p against the boiling point at 760 mm., which is the basis of G. Granger Brown's [7] chart for pure hydrocarbons. This method is also used in the present paper for the boiling-point conversion chart.

Vapour Pressure of Mixtures.

The vapour pressure of a pure substance is quite a definite idea, but that of a mixture of substances such as a petroleum product requires definition if ambiguity is to be avoided.

If the pressure at which such a product is in equilibrium with its own

vapour is measured, that pressure is actually due to the sum of the vapour pressure of the hydrocarbons in the product and the partial pressure of dissolved air and water. In this paper the hydrocarbon vapour pressure only is dealt with, and the method of measurement purposely excluded the other.

As is well known, the vapour pressure exerted by a mixture decreases as the ratio of the volumes of the vapour phase to that of the liquid phase is

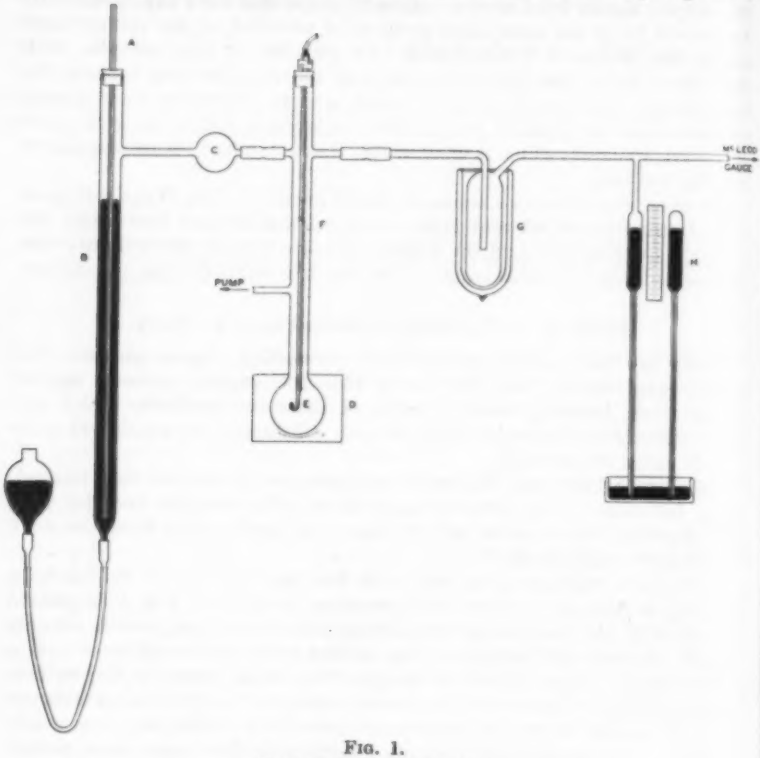

FIG. 1.
BOILING-POINT APPARATUS.

increased, owing to the larger proportion of lighter constituents in the vapour phase. This ratio was kept small enough in these experiments for this effect to be negligible, as is shown later.

It should be mentioned that the routine commercial vapour-pressure tests, such as the "Reid," bear no exact relation to the true vapour pressure, and are therefore excluded from the present discussion.

EXPERIMENTAL METHODS.

For the determination of vapour pressures of atmospheric and below, the "Boiling-Point Apparatus" was used (shown in Fig. 1). This

apparatus consisted of a flask of small capacity (70 ml.) with a long, wide neck which constituted the condenser. For higher temperatures, air cooling was sufficient. At low temperatures a cooling jacket (not shown in Fig. 1) was fitted. Kerosine and solid CO_2 or water were used as the cooling media. Attached to the top was a manifold, *F*, consisting of a glass tube about 12 in. long and $\frac{3}{4}$ in. I.D. with connections to the pump, vacuum gauge and leak, *B*. The purpose of the latter was to allow a small flow of air down the tube from the leak to sweep away any condensable material from the McLeod gauge, which was used to measure the lowest pressures. The latter was also protected by a CO_2 trap, *G*. For pressures of 1 mm. and above, the manometer, *H*, was used; lower pressures were read on the McLeod gauge. The system was evacuated by a two-stage diffusion pump or a rotary oil pump, depending on the working pressure desired. The pressure was controlled by adjusting the leak and the choke on the suction line to the pump.

The flask was heated electrically and placed in a small lagging box, *D*, and the whole arrangement could be gently shaken. The tip of the iron-eureka thermocouple, *E*, was placed just above the surface of the liquid (when hot), and was kept wet by the agitation.

The thermocouple was calibrated at the boiling points of water, naphthalene and sulphur, and the temperature was read on a Cambridge Suspended Indicator calibrated at 10° C. intervals. It was constructed from wires very carefully selected for their uniformity, and was calibrated at regular intervals and found not to have varied from beginning to end of the experiments.

The leak consisted of a fine capillary, *A*, the pressure drop across which could be controlled. A capacity, *C*, of about 1 litre was included to prevent pressure surges. The quantity of air necessary to give a linear velocity of roughly 15 cm. a second in the 2-cm. diameter manifold was calculated, and the leak adjusted to this rate. By calculation, this velocity gave a negligible pressure drop, and this was proved to be so by varying the rate of leak, and observing the boiling point of a sample when boiling under constant pressure as measured by the McLeod gauge.

Effect of Vapour Space.—In this apparatus the volume of the vapour phase is comparatively large, and there is also a certain amount of condensed vapour held up in the reflux condenser, which is exactly equivalent to enlarging the vapour space still further.

For this reason, this type of apparatus is not suitable for determining the true hydrocarbon vapour pressure of samples which may contain small amounts of dissolved hydrocarbon gases or traces of components very much more volatile than the bulk of the sample.

However, for cuts of definitely restricted boiling range such as were examined for this paper, the effect of the vapour space was shown to be negligible by preliminary experiments on cuts of very much wider boiling range (four or five times as great), which themselves showed negligible error from this cause.

Effect of Heat Input.—The effect of varying the heat input to the flask was investigated, and it was found that the temperature in the liquid remained constant to within 1° C. over a wide range of heat input. For instance, when refluxing a narrow cut from lubricating oil under 0·16 mm.

pressure, the following temperature readings were obtained with various values of heater current :—

Total Watts.	Net Watts to Oil (= Total watts less heat loss).	Temp., °C.
12·5	0	150–170
15·1	2·6	183
18·0	5·5	183¾
21·0	8·5	184
24·5	12·0	184¼
28·0	15·5	185

The importance of this observation is that it shows that the results with this apparatus cannot be in error due to pressure drop in the apparatus or to variations in the quantity of condensed vapour held up in the reflux condenser.

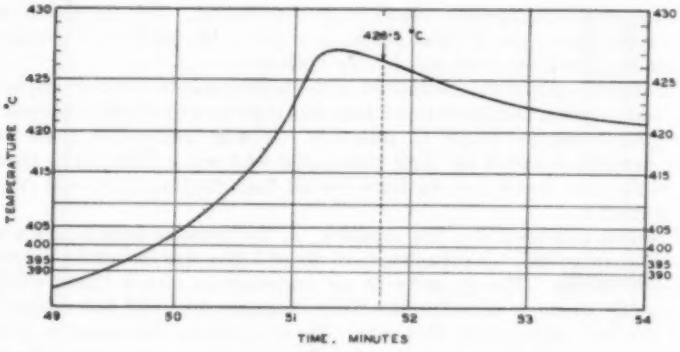

FIG. 2.

Area below curve between ordinates 51¾ minutes and 54 minutes = 101 sq. cm., which corresponds to a drop of 5·5° C. in b. pt.

Area below curve between ordinates 49 minutes and 51¾ minutes = 86·5 sq. cm., which indicates that the b. pt. will have dropped $5{\cdot}5 \times \frac{86{\cdot}5}{101} = 4{\cdot}7°$ C. Hence true b. pt. = 426·5 + 4·7 = 431·2° C.

Allowance for Cracking.—At the higher temperatures, it is necessary to allow for the effect of cracking on the boiling point. Assuming that only a small amount of cracking has taken place, the fall in boiling point will be proportional to this amount, and the true boiling point of the uncracked material may be estimated by taking the time–temperature curve while heating up to the boiling point, and while the boiling continues for some time. During the latter period, the temperature gradually falls owing to the occurrence of cracking. The effect on the boiling point of cracking during the heating-up period is then estimated by plotting the time–temperature curve as shown in Fig. 2. It was known from previous experiments that in this region the rate of reaction is doubled for a temperature rise of 13° C., and the temperature scale was drawn in accordance with this law. The area under the curve of Fig. 2 between any two values of

T is then proportional to the amount of cracking taking place during this period; that is, to the drop in boiling point, if our initial assumption is correct. For the case shown on Fig. 2 which was plotted from the experimental results on a narrow cut from lubricating oil at 760 mm., the addition which had to be made to the observed boiling point was 5·5° C. The validity of this method of correcting the boiling point for cracking may be checked by making a similar calculation to that shown below Fig. 2, but using as a starting point for the calculation a different time after boiling has started. For example, the areas below the curve between the ordinates 52¼ and 54 minutes, and between 49 and 52¼ minutes, may be used to calculate the addition which should be made to the observed boiling point at 52¼ minutes. The corrected temperatures so obtained should be the same whatever time is chosen as long as boiling has definitely started, and it is found that this is so within the limits of experimental error.

The adjustment to the observed temperature was of any magnitude only in some three of four experiments, and it was found that the method gave excellent repeatability.

Samples Tested.

In order to extend the vapour-pressure data for hydrocarbons to higher molecular weights, a number of cuts of narrow boiling range (roughly 20° C.) was prepared. These were obtained by distilling residue from Iranian crude or untreated dewaxed lubricating oil stock under a pressure of 1 mm. of mercury using a column 18 in. long packed with ¼-in. Lessing rings.

Suitable cuts were selected, and the vapour-pressure curves up to 760 mm. were determined in the boiling-point apparatus. These cuts are distinguished by the mean boiling point observed during the distillation converted to 760 mm. by means of the chart shown in Fig. 5.

In addition to these cuts, a sample of *n*-dodecane was prepared,* and the vapour-pressure line from 0·15 to 760 mm. was determined in the boiling-point apparatus, and from 760 mm. to the critical in an apparatus similar to that of Young.[4]

Table I.

Narrow Boiling-Range Cuts from Persian Crude.

J. Mean boiling point 295° C.		K. Mean boiling point 365° C.		L. Mean boiling point 382° C.	
Pressure, mm. Hg.	Temperature, °C.	Pressure, mm. Hg.	Temperature, °C.	Pressure, mm. Hg.	Temperature, °C.
5·2	138	2·7	179	1·6	181
12·2	156	10·4	207	12·0	230
14·2	160	23·5	229	13·1	234
99	212	46·5	253	38·7	265
237	243	102·2	279·5	84	291
336	257	205	307	252	334
507	274	408	337	502	365
757	293	756	366	760	385

* See Appendix.

This material was chosen, as it has a critical point which is at about the highest temperature at which a trustworthy experiment can be carried out. The full results are included in the table and in Fig. 4, on account of the general interest, although only the vapour pressure up to 760 mm. is of importance in connection with the work described in this paper.

The experimental results are shown in Tables I to III.

TABLE II.

Narrow Cuts from Unrefined Lubricating Oil.

M. Mean boiling point 430° C.		N. Mean boiling point 440° C.		O. Mean boiling point 477° C.	
Pressure, mm. Hg.	Temperature, °C.	Pressure, mm. Hg.	Temperature, °C.	Pressure, mm. Hg.	Temperature, °C.
0·75	207	0·16	184	0·25	215·5
1·95	227·5	2·85	242	0·8	246
2·0	227	4·95	254·5	3·15	271·5
8·1	259	5·65	259	9·8	304
9·0	260	10·0	269·5	36	345
30·1	297·5	50·0	323	205	412
33·7	299·5	101·5	349	—	—
87·5	334·5	208	377	—	—
91	335·5	314	392	—	—
287	382·5	760	441	—	—
760	431·0	—	—	—	—

TABLE III.

n-Dodecane.

Pressure, mm. Hg.	Temperature, °C.	Pressure, mm. Hg.	Temperature, °C.
0·148	27	366	185
4·5	79	437	190
10·1	92	756	215
11·4	95	1,040	228·5
20·2	114·5	1,492	246
32·7	117·5	2,960	284·5
54·5	128·5	5,865	325
96·8	145	9,960	359·5
109·8	147	11,540	378
224	169·5	13,300	385 critical
346	184·5		

CONSTRUCTION OF THE BOILING-POINT CONVERSION CHART.

The data in Tables I to III were plotted on Log $P - \frac{1}{T}$ scale (Method 1 above) as shown in Fig. 3 for sample *N*. Points from the smoothed lines on these graphs, together with points for pure hydrocarbons, were plotted according to the second of the two methods mentioned above to give Fig. 4, the lines shown being for pressures 0·1, 1·0, 10, 100, 1000, 10,000 mm. Hg. and the critical. The vapour-pressure curves for the narrow cuts were extrapolated to 0·1 mm. to give the first of these lines.

It will be observed that in this chart the pressure lines are curved at the lower end, but that at the higher temperatures they become straight, and this is the case over a wide enough range for it to be assumed that they may be extrapolated with confidence. The line for 1 mm., for instance, is straight from an atmospheric boiling point of 280–480° C., which is the upper limit of the figures available.

A boiling-point conversion chart was constructed from Fig. 4 by extrapolating the family of straight lines to an atmospheric boiling point of 700° C., and the pressure range carried down to 0·01 mm. Hg. The

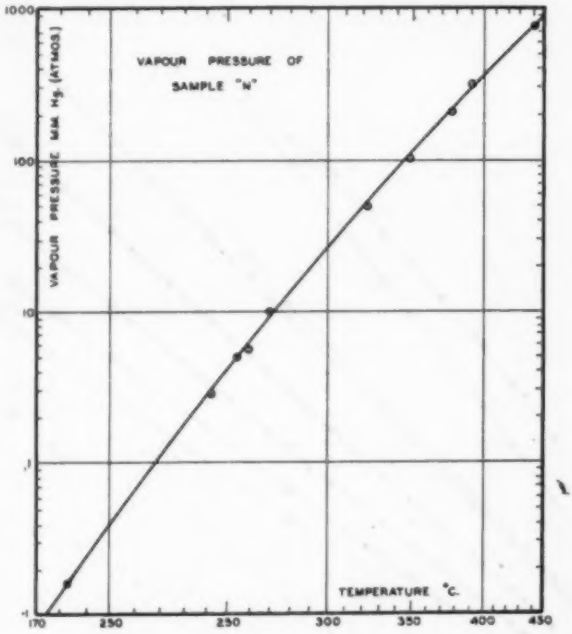

FIG. 3.

nomogram (Fig. 5) was constructed from this chart, as the chart itself is useful only if reproduced on a very large scale.

This method of conversion has been used extensively in these laboratories for converting temperatures in vacuum distillations, and in addition to having proved entirely satisfactory in service, it has been checked by comparing distillations carried out at 760 mm. with those carried out at 10–50 mm. and distillations at 2 mm. with those at 0·03–0·05 mm. in special apparatus which ensures reliability of the pressure measurements. The agreement between the converted boiling-point curves was excellent in every case.

It should be particularly noted that a chart of this sort, which is constructed for pure hydrocarbons and narrow cuts, cannot be used for

determining the vapour-pressure line for residues or for distillates of wide boiling range.

Experience shows that a boiling range of 60° C. is about the limit for which the chart can be used without substantial error. The chart is, therefore, applicable to the conversion of boiling points at the still head in

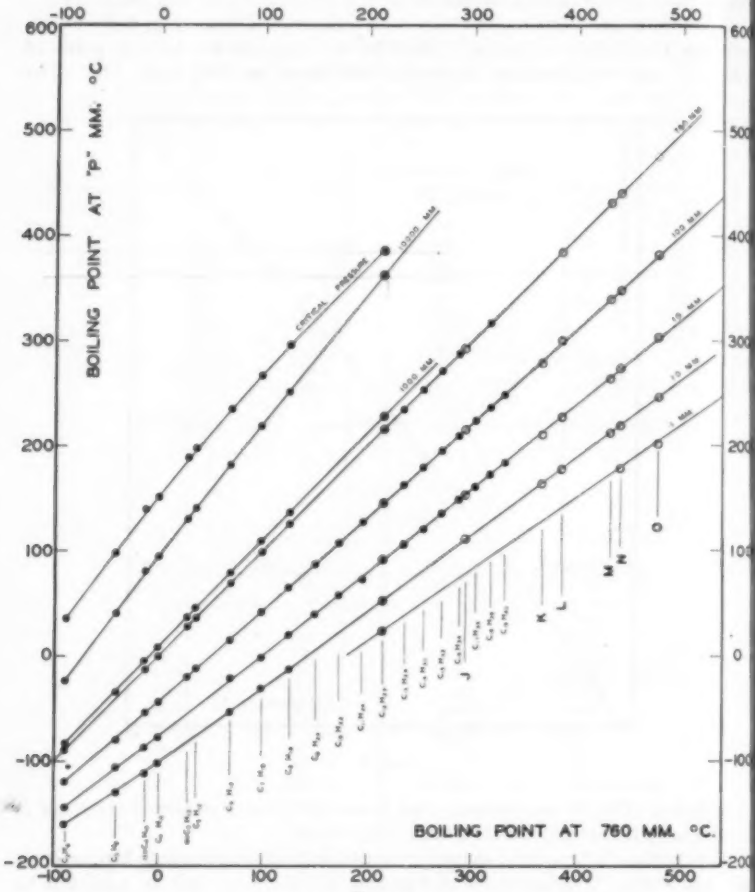

FIG. 4.

all cases, but not to the conversion of the still temperatures unless the charge is of narrow boiling range.

COMPARISON WITH PUBLISHED DATA.

The chart was compared with the formula proposed by Ashworth,[1] and with the chart recently published by Watson and Wirth.[8] The results of the comparison are shown in Tables IV and V.

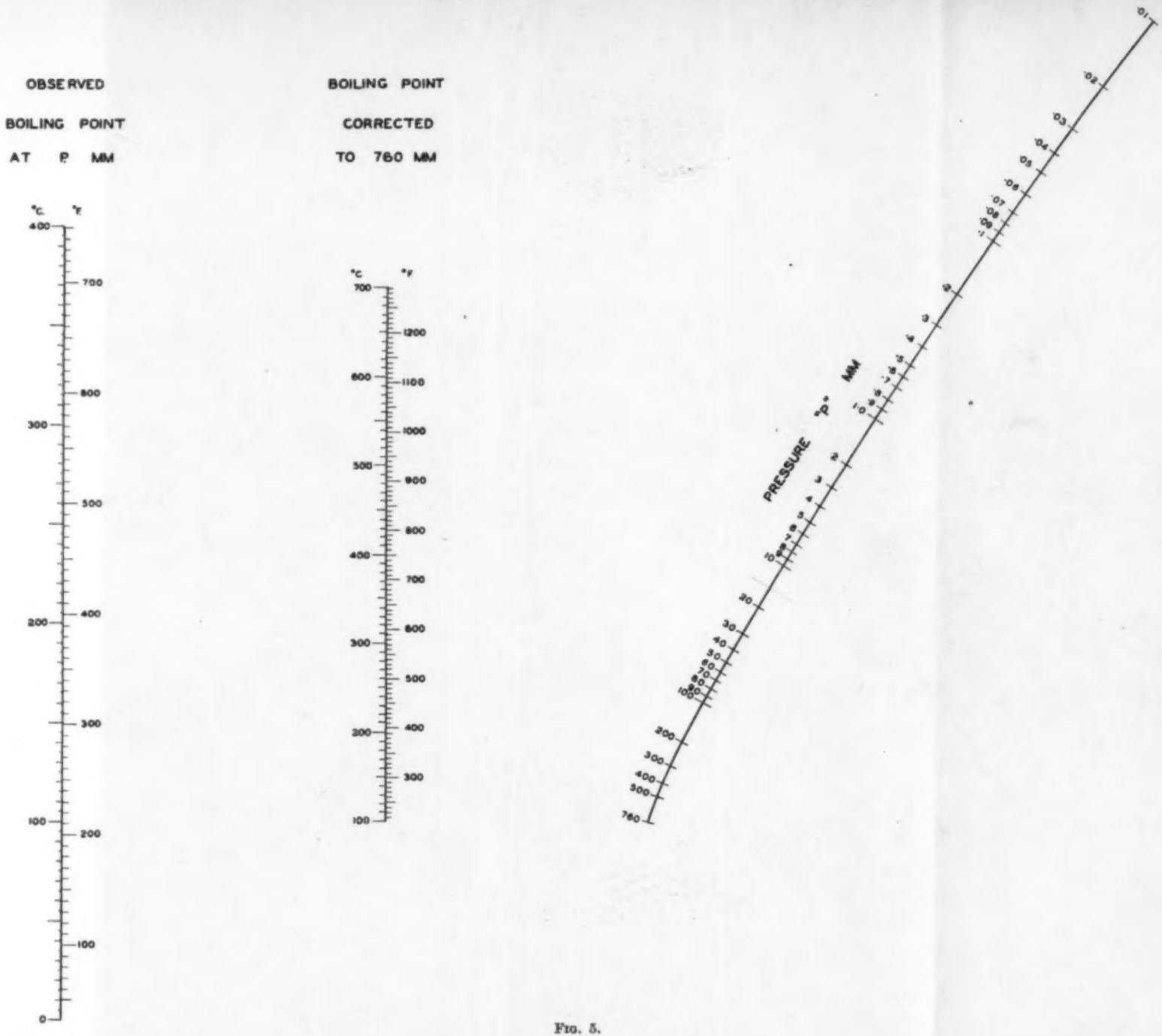

FIG. 5.

UNIV OF MICH

TABLE IV.

Observed b. pt., °C.	Pressure, mm.	B. Pt. °C. Converted to 760 mm. by:	
		Ashworth's Formula.	Present Chart.
407	100	500	503
330	10	500	511
272	1	500	510
227	0·1	500	510
190	0·01	500	507

TABLE V.

Observed b. pt., °F.	Pressure, mm.	B. Pt. °F. Converted to 760 mm. by:	
		Watson and Wirth.	Present Chart.
300	100	428	430
	10	553	552
	1	648	653
	0·1	718	748
	0·01	768	829
500	100	647	650
	10	785	797
	1	887	922
	0·1	953	1039
	0·01	1005	1142
700	100	872	872
	10	1012	1044
	1	1112	1190
	0·1	1180	1332

The agreement with Ashworth is good, particularly in view of the fact that the method used in extrapolating in the two cases was widely different, and that nonadecane (b. pt. 330° C. at 760 mm.) was the highest-boiling liquid the vapour-pressure line of which was used in the derivation of his formula.

The divergencies from the chart of Watson and Wirth are greater, particularly at the lower pressures. The divergence from the chart published by Granger Brown and Coats[9] is of the same order, which is to be expected, since it is to a great extent the basis of the chart of Watson and Wirth.

We have carefully considered the discrepancy between our chart and Watson and Wirth's in the light of possible errors in the experiments described in this paper. Supposing these errors have not been completely eliminated in our experiments, correction for them will only have the effect of increasing the divergence between the charts, and for this reason, we feel that the method of extrapolation used by Watson and Wirth is not reliable.

The authors are indebted to the Chairman of the Anglo-Iranian Oil Company Limited for his permission to publish this paper.

APPENDIX.

Preparation of *n*-Dodecane.

We are indebted to Dr. S. F. Birch for the sample of *n*-dodecane used. The method of preparation was as follows: *n*-Hexyl alcohol was prepared from *n*-butyl magnesium bromide and ethylene oxide by the method described in "Organic Syntheses," Vol. VI, p. 54, and converted into the corresponding bromide (cf. *ibid.*, Vol. I, p. 5).

The carefully purified bromide was converted into *n*-dodecane as follows:—Sodium (57 g.) was powdered under toluene in a round-bottomed flask in the usual way, the toluene being replaced when cold by decantation with dry ether (300 ml.). An efficient reflux condenser was attached and some *n*-hexyl bromide added, when after a few minutes a violent reaction set in. When this slowed down, the contents of the flask were kept vigorously boiling by adding, fairly rapidly, more bromide in portions of 10–15 ml. until a total of 272 g. had been added. The whole was then allowed to stand over-night, and next day refluxed for 2 hrs., after which it was again allowed to settle over-night. The following day the supernatant layer was poured off and the residual sodium bromide thoroughly washed with dry ether, the washing being added to the main bulk. After removing most of the ether by distillation through a long column, the residue was refluxed with fresh sodium for several hours. Finally it was distilled, the low-boiling portions being rejected and the remainder collected as crude *n*-dodecane (yield 96 g. = 68·5 per cent. of the critical). It was purified by treatment with sulphuric acid, neutralization, drying over calcium chloride and finally distillation over sodium.

References.

[1] Ashworth, *J.I.P.T.*, 1924, **10**, 787.
[2] Cox, *Ind. Eng. Chem.*, 1923, **15**, 592.
[3] Maxwell, *ibid.*, 1932, **24**, 502.
[4] Young, *Sc. Proc. Royal Dublin Soc.*, 1909, **12**, 389.
[5] Krafft, *Ber.*, **15**, 1721; **29**, 1323; **32**, 1623.
[6] Wilson and Bahlke, *Ind. Eng. Chem.*, 1924, **16**, 115.
[7] G. G. Brown, *Proc. Nat. Gas Ass.*, 1928, 43.
[8] Watson and Wirth, *Ind. Eng. Chem. Anal.*, 1935, **7**, 72.
[9] Coats and Brown, "A Vapour-Pressure Chart for Hydrocarbons." Dept. of Eng. Research, Univ. of Michigan. Circular Series No. 2 (Dec. 1928).

THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

TRINIDAD BRANCH.

THE Forty-third General Meeting of the Trinidad Branch of the Institution of Petroleum Technologists was held at the Apex Club, Fyzabad, on March 28th, 1935, the chair being taken by Commander H. V. Lavington, R.N., Branch Chairman.

The following paper was presented :—

TREATMENT OF WATER FOR DOMESTIC PURPOSES IN A TRINIDAD OIL-FIELD.

By A. H. RICHARD, A.C.G.I., B.Sc., A.M.Inst. C.E. (Member).

SYNOPSIS.

The main object of the paper is the description of a water purification plant such as is considered necessary for isolated camps.

Sedimentation need not be specially provided for.

Coagulation requires careful consideration.

Filtration is easily taken care of.

Sterilization and removal of tastes and odours will probably seldom be necessary.

Sulphate of alumina is the surest and easiest coagulant so far available.

Experimental determination of dose and optimum conditions for flocculation are discussed.

Practical details are given, with particular reference to a simple automatic dosing chamber, and a cone type coagulating basin.

INTRODUCTION.

IN countries such as Trinidad, where oil-field camps are generally inaccessible from established sources of pure water, a local supply is of first importance.

Rain stored in concrete cisterns will usually provide drinking-water, but cannot be relied on for all domestic purposes.

The deficiency must be made up from the field system which is more often than not drawn from a river or stream, either direct or after storage in open reservoirs. In certain cases such water may be used without treatment for bathing and washing, but will almost invariably be very turbid and polluted with bacteria (see Appendix I), and in the interest of the health and general well-being of the community it will be policy and economy to instal a purification plant.

It may not be generally realized that it is comparatively cheap and simple to erect and run such an installation, the description of which is the main object of this paper.

General Considerations.

The subject may be considered in five main divisions :—

(1) Sedimentation.
(2) Coagulation.
(3) Filtration.
(4) Sterilization.
(5) Taste and odour removal.

1. *Sedimentation.*—By reduction of velocity through settling basins, silt and other readily falling particles are dropped out. These are usually present only in water from streams in spate, the incidence of which will not normally justify basins for that purpose alone.

The storage reservoirs which are essential to oil-field operations provide enormous sedimentation capacities.

2. *Coagulation.*—This stage is the removal of fine suspensions and organic and colouring matter, which are carried down by a hydroxide precipitate formed in the water from the reaction of added chemicals. The hydroxide coalesces or flocculates into larger aggregates of gelatinous particles, the mass being commonly called the floc. Pre-sedimentation will reduce the quantity of coagulant required.

The process is a special case of filtration, the medium being passed through the water, and in so doing obeys the laws of sedimentation.

A substantial removal of bacteria is always effected (see Appendix I).

Coagulation will be considered in more detail later.

3. *Filtration.*—Very low turbidity and colour are removable without prior coagulation. In other cases the chemical is injected into the water immediately before the filter, and the two processes occur simultaneously.

With high turbidities pre-coagulation is essential, as the volume of floc will be too great to allow of reasonable filter runs.

The filter then serves to remove the finer floc particles, as well as further reducing the bacteria.

Economical distribution of the work is a matter for local consideration. In Trinidad pre-coagulation is imperative.

The modern rapid pressure filter, because of compactness, ease of operation and low maintenance, will obviously be chosen rather than the cumbersome, slow, open-basin type. The engineer thereby benefits from the manufacturer's experience, and relieves himself of design and construction. The only specification needed is the maximum rate of flow.

Filters are washed by reversed flow of clean water, accompanied by agitation of the sand bed either by mechanical means or compressed air. The frequency is determined by a balance between efficiency and consumption of wash water.

4. *Sterilization.*—As will have been seen, the logical point for the destruction of the remaining undesired bacteria, if any, is after filtration. Also, turbidity in unfiltered water would waste disinfectants.

The most widely used agent is chlorine, which may be applied either as bleaching-powder or more generally in the liquefied form.

The criterion of effective sterilization is a minimum of residual chlorine after a given time—0·1 to 0·2 p.p.m. after 10 minutes' contact.[1] Deter-

mination is by the *ortho*-toluidine test, a convenient form being colour comparison against graduated standards.

Too high a residual will give an objectionable taste.

There has lately been considerable use of ammonia with chlorine, the advantages claimed being the reduction of after taste and odour, thereby allowing higher chlorine residuals to be carried. The technique and benefits are far from being established.

In the plant with which the author has been connected, coagulation and filtration have been so effective in removal of bacteria that the need for sterilization has not arisen (see Appendix I). It is believed that this will be the normal experience in similar districts of moderate rural population.

Should the occasion arise—as, for example, during an epidemic—it is felt that the use of liquid chlorine alone will be the simplest and surest method. The suppliers will no doubt advise on and furnish the appropriate dosing apparatus.

Equipment for small supplies is described by Cox.[2]

Frequent bacteriological examination is necessary whether sterilization is resorted to or not.

5. *Removal of Odours and Tastes.*—The well-known adsorptive property of activated charcoal has resulted in its extensive use in this field.

It is not believed that a nuisance of any importance will be found at those plants which this paper envisages.

Should such occur, simple pressure filtration through granular and/or powdered charcoal is recommended.

Coagulation in Detail.

This branch of the treating cycle, being most susceptible to variation to meet local conditions, calls for experiment and careful design.

There are three main coagulants :—

(1) Ferrous sulphate.
(2) Sulphate of alumina.
(3) Sodium aluminate with sulphate of alumina.

1. *Ferrous Sulphate.*—Ferrous sulphate reacts to form ferric hydroxide, $Fe_2(OH)_6$ giving a heavy quick settling floc, very well adapted to coagulation. But as it is necessary to add lime or other substances to obtain reasonable speed of action, it has not found as much favour as the single chemical sulphate of alumina process.[3] In the words of Parker ". . . the supervisor . . . is generously allowed two chemicals . . ., in place of one, to make mistakes with. . . ."

There is a possibility of iron producing highly coloured bodies with tannin compounds [4] which may be present in the water.

The author was unable to obtain anything approaching a satisfactory precipitate, and believes that ferrous sulphate will not be found generally as suitable or reliable as sulphate of alumina.

Recently the process has been receiving more attention and difficulties have been overcome.[5]

2. *Sulphate of Alumina.*[6]—Often referred to as alum. The reaction is : $Al_2(SO_4)_3,18H_2O + 3Ca(HCO_3)_2 = 3CaSO_4 + 2Al(HO)_3 + 6CO_2 + 18H_2O$,[1]

giving a large, ready settling floc. Having obtained approximate dosages, the treatment is easy to handle and to vary according to requirements.

Liberation of CO_2 improves the palatability of the water, but as temporary is converted into permanent hardness, it is less suitable for boilers and other industrial purposes. It can be softened by lime or soda, *e.g.*: $CaSO_4 + Na_2CO_3 = Na_2SO_4 + CaCO_3$.[2]

As the water at the end of equation (1) is on the acid side, the neutralization effected by (2) is of advantage. A typical case is given as under :—

Raw water	*p*H 7·5
After coagulation with 8 grains of sulphate of alumina per gallon.	*p*H 5·2
After neutralization with 5 grains of soda per gallon . .	*p*H 7·1

In the author's experience a *p*H of 5·2 in the finished water gave no signs of corrosion in the delivery system, consisting of galvanized clear-water tanks and galvanized pipes, over a period of seven years. At that time one of the two tanks, on being opened up, showed considerable corrosion over a two-foot band which lay between wind and wave due to daily fluctuation in level. The other tank, which was constantly full, was in excellent condition, as also a section of the pipe-line removed for inspection.

Although not considered vital, it was thought advisable to neutralize, particularly as water from the plant was to be used for gas-engine cooling-water make-up.

Addition of soda before or with alum is uncertain and unsatisfactory, very often interfering with proper coagulation, and leaving the water with a milky finish, which persists after filtration.

The lime or soda should be introduced at a point a little after flocculation has taken place. Any residual alum is precipitated and settlement of the fine floc assisted.

Soda treatment as above must not be confused with a double chemical dose : the amount of soda has no influence on coagulation, and may be varied widely without affecting the finished water to any marked extent.

Quality of Alum.—Sulphate of alumina is represented by $Al_2(SO_4)_3,18H_2O$, and contains 15 per cent. by weight of Al_2O_3 and 36 per cent. of SO_4. In basic alum Al_2O_3 (soluble in water) is increased to 17 to 18 per cent. and is superior as a coagulant, and there is a minimum consumption of alkalinity in the water.[7]

The author recommends iron-free alum for reasons given above, the small extra cost being justified by the avoidance of the possibility of discoloration.

3. *Sodium Aluminate with Sulphate of Alumina.*—Sodium aluminate is extensively used for water softening and is finding an increasing field for coagulation.

The reactions are :—[8]

$$Na_2Al_2O_4 + 2CO_2 + 4H_2O = 2NaHCO_3 + 2Al(OH)_3. \quad (I)$$
$$6NaHCO_3 + Al_2(SO_4)_3 = 3Na_2SO_4 + 2Al(OH)_3 + 6CO_2. \quad (II)$$

Little, if any, neutralization is required, and amongst other advantages claimed, an overall saving in cost of treatment is obtainable.

The author's experiments with sodium aluminate have not progressed sufficiently to allow of a deduction.

As it will be seen from the foregoing that coagulation with alum is the easiest method, this will be further considered to the exclusion of the others.

Experimental Determination of Dose.

A chemical analysis is not essential.

The accepted method of experimental determination for a particular water is by what is known as the Jar Test, in which varying quantities of chemical are added to samples of the water in glass jars, and results noted.

The author has found 500 ml. in a graduated glass cylinder, of about 2 in. diameter × 10 in. depth of water, to be convenient. The chemicals are made up into solutions of such strength that unit volume of solution represents a unit of dose measurement. For instance, using grains per gallon, the solution will be made up so that 1 ml. will contain 500/4544 of a grain of chemical, and when added to 500 ml. of water will give a dose of 1 grain per gallon.

A series of jars will be set up simultaneously, and dosed with progressive strengths and combinations of chemicals Immediately after dosing, the water is vigorously stirred for a second or two, and then allowed to stand. It is generally realized that uniformity of stirring should be observed.

The author's criteria for a satisfactory dose are :—

1. Floc must begin to form within 5 minutes.
2. Flocculation must then proceed rapidly and be complete in about 20 minutes from dosing.
3. Settlement must be complete in from 1 to 2 hours from dosing, the water being crystal clear.
4. If any milkiness develops within 1 to 2 days, the dose is too small or otherwise unsatisfactory.

It has been found that there is a minimum dose for a given water. A slight underdose will not precipitate completely even after extended settling. Milkiness due to later precipitation of residual alum will appear after filtration.

Within limits, an overdose will not produce undesirable effects, and must be very large to appear in the finished water.

Nolte and Kramer [9] in an excellent paper give results of various rates and times of stirring and shaking, and conclude that velocities of 0·5–1·5 ft. per second for 30 minutes are best, and recommend these conditions for plant operation.

By this method the author could not obtain any appreciable improvement on the minimum previously found.

Confirmation of a minimum dose has since been furnished in a paper by Smith,[10] who further states that no amount or kind of mechanical treatment can overcome the failure to provide the minimum.

Optimum Conditions for Flocculation.

Batch coagulation is practically obsolete, and with proper conditions a continuous system, besides having greater capacity for the same outlay and space occupied, will show economies in chemicals.

Quiet water is not ideal. The author prefers something between the

quiet swirling motion advocated by Parker [7] and the velocities recommended by Nolte and Kramer.[9]

For local conditions such velocities are necessary for thorough mixing, but should not continue for more than 5–10 minutes—that is, the velocity should be considerably reduced almost as soon as the floc has started to form, otherwise it will be too much broken up.

For the same reason, the author feels that the excellent system of paddles in the Dorr Flocculator—described by Smith [10]—would not be applicable to local conditions as such.

It has been abundantly demonstrated that a judicious system of baffles will improve results. Smith's objection to baffles is the loss of head, which is due to maintaining fairly high velocities for an extended travel.

The author's development of baffles has led to a realization that probably their most essential function is to prevent dilution of the chemically charged water entering the system until the reactions are complete.

In what the author therefore terms the reaction chamber a good but not violent mixing is necessary. Beyond this point quiescence should commence.

It was at one time thought that there was an optimum *p*H for best flocculation, but this has not been found to hold. The source and particular condition of the water are all-important, and here knowledge gained by experience is the deciding factor.

Peterson and Barton,[4] as a result of extensive experiments, find that *p*H is less the controlling factor than salt content, and suggest that variations are more probably due to sulphates.

The author has been unable to find any other explanation for the high dose and difficulty of treatment for the Cunapo River water (Appendix II) than that the sulphate is higher.

Parker [11] recommends a split dose, which, however, the author cannot substantiate. The effect is equivalent to an underdose, and is not made good by addition of the remainder.

Practical Details.

General Layout.—Incoming raw water is metered, admitted through a float valve into a dosing chamber, then flows by gravity to the coagulating basin, the level in which is controlled by the valve.

The basin may be in two parts, the level in the first being constant, and in the second fluctuating according to demand. If the latter, the take-off to the filters will be by means of a floating swing pipe.

The coagulating basin should be about 30–40 ft. above the filters, to give sufficient reserve of gravity head.

From the filters the water passes through a float-valve level control to the clear well or tank, preferably a concrete cistern, from where it is delivered to the mains.

The maximum demand rate has been found to be $2\frac{1}{2}$ times the 24-hourly average. The capacities of the clear well and of the filter may be adjusted to an economical balance. The filter outlet must be pinched so that flow never exceeds the maker's maximum rating, otherwise filtering efficiency will be lost.

Wash water for the filter is pumped from the clear well.

Dosing Chamber.—There are many excellent mechanical dosing methods available, most of which feed a solution of the chemical through a needle valve by means of the differential pressure created by the flow of water across an orifice or through a venturi.

For a small plant the needle valve opening is so fine that it cannot be kept clear, and was found to be quite unworkable. Alum is strongly

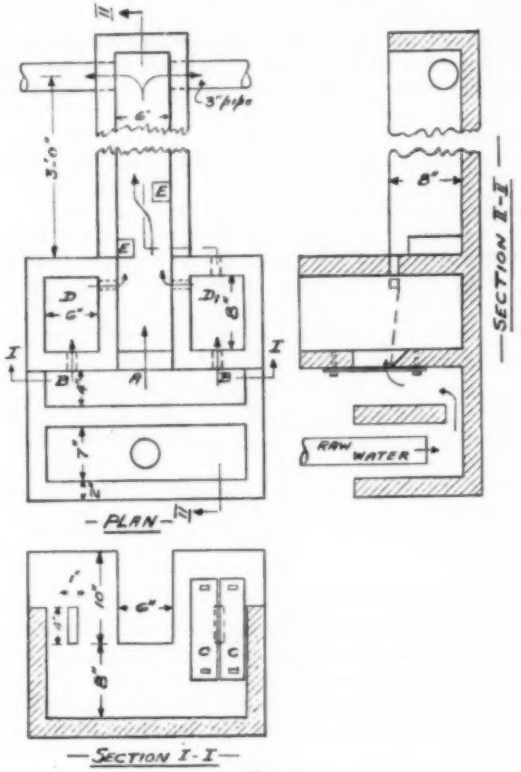

FIG. 1.

WEIR TYPE AUTOMATIC CHEMICAL DOSING CHAMBER.

corrosive, and all parts in contact must be of brass—even this will corrode.

Other forms employ set adjustments and are not automatic.

The author has developed the weir-type dosing chamber described below and illustrated in Fig. 1, for particular application to small plants.

The sills of main weir, A, and of the proportioning weirs, B, are at the same height. The volumes of the side streams are adjusted by sliding the plates, C, forming the sides of the weirs, B. D, D_1 are the chemical com-

partments. The solutions re-entering the main stream are thoroughly mixed by baffles, E, before the stream is divided. The alternative outlet from D_1 is provided for taking a solution to another point in the system.

If the quantity of chemical standing in the compartments is never allowed to fall below liquid level, and if the size is adequate, a fully saturated and therefore constant strength solution is delivered, the volume or dose being regulated by the adjustable weirs.

In larger plants, an underflow baffle wall may be placed before the chemical chamber outlets.

In small plants of, say, less than 100,000 gallons per day, it may be that the adjustable weir will be too narrow when delivering a saturated solution. In such cases the bottom of the compartment will be filled with concrete

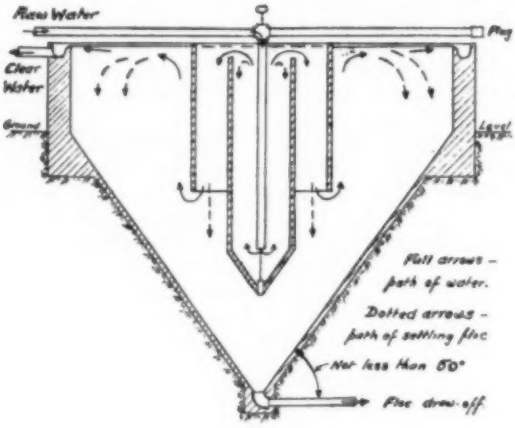

FIG. 2.

CIRCULAR CONICAL COAGULATION BASIN.

to the sloping dotted line. A semi-saturated solution will result, not of absolutely uniform strength, but sufficiently so for practical purposes. The compartment must always contain some chemical.

The height above liquid level or dotted line should contain not less than 4 hours' supply of chemical, and may be made sufficient for 24 hours if desired.

In small sizes the walls must not converge downwards, or the chemical will arch and not follow down. Powdery chemicals, *e.g.* soda ash, should be briquetted to avoid arching due to crystallization.

The chamber is made of concrete, the only metal being the adjustable plates which are not in contact with alum. There is therefore no corrosion trouble. Cost is a minimum. Adjustments are simple and visible. The complete functioning of the apparatus is open to inspection. Replenishment of chemical is reduced to the simplest. Maintenance is nil.

The author sees no reason why this arrangement should not be equally applicable to the largest plants, in place of the expensive and complicated equipment now used.

The dimensions given in Fig. 1 indicate a size suitable for a plant for about 50,000 gallons per day.

Coagulating Basin.—As a result of previous experience, the cone type of basin shown in Fig. 2, which was proposed by Col. Hickling, has been developed.

The conical portion below ground level is lined with 1 to 2 in. of fairly rich cement-sand grout plastered about a rabbit-wire basis.

The circular baffles are similarly constructed, the rabbit wire being secured to a skeleton frame of 1-in. pipe, the whole being suspended from radial supporting members across the top of the cone. This method is better than supports resting in the ground, as it leaves the apex of the cone unobstructed.

A circular launder is formed in the top of the vertical wall. As the height of water over the weir into the launder is very small, it is difficult to secure uniform flow all round, and sectional weirs with blanks between, say 2 in. of weir and 4 in. of blank, will be preferable.

The water level in the launder is communicated to a chamber for the float of the valve which controls the inlet to the dosing chamber.

The plant is best situated on the top of a hill with a steep slope on at least one side, which can be bored through for insertion of the floc draw-off pipe.

The following dimensions are suitable for a throughput of 25,000 gallons per day :—

Circular portion above ground level—13 ft. diam. × 3 ft. high.
Cone—9 ft. deep giving a slope of 53°.
Centre baffle chamber—2 ft. diam. × 8 ft. deep, with a 6-in. over the top flow space.
Outer chamber—4 ft. 6 in. diam. × 5 ft. deep.
Launder—approximately 4 in. × 4 in. with rounded bottom.
Inlet pipe—3 in. galvanized.
Outlet pipe—4 in. galvanized.

The plug at the bottom of the centre chamber is attached to a rod passing through the down pipe, and is withdrawn for cleaning and to equalize the pressure when filling and emptying.

The centre baffle is the main part of the reaction chamber previously referred to, and the average retention is 9 minutes, the balance of reaction taking place in part of the outer chamber to an extent depending on the momentary flow.

The average upward velocity in the centre chamber is just under 1 ft. per minute, which is more than sufficient to lift the floc. The falling velocity of floc is 5 in. per minute and velocity of water necessary to lift is 5·5 in. per minute.

Actually through short circuiting and because of some air entrained in the down pipe, there is a much greater rising velocity immediately around the down pipe, which is beneficial. As a consequence, some of the floc is carried down the outer part of the inner chamber, and recycles with the rising water. Though unintentional, this appears to be useful, the effect being similar to that of the Dorr Flocculator previously mentioned, a feature of which is controlled return of a portion of the floc to the incoming water.

About 75 per cent. of the floc settles direct from the mouth of the outer chamber. The remainder which is carried over commences to settle as indicated, when, due to enlarging diameter, the horizontal velocity falls below the critical carrying velocity, which has been found to be 18 in. per minute.

In the plant at which two of these cones were constructed, the two original batch coagulating tanks are used as secondary basins, but are practically unnecessary, They help to smooth out diurnal fluctuations of demand.

In demonstration of the relative merits of the two systems, the two former batch tanks with a cubical capacity of 14,000 gallons each reached a maximum combined throughput at 25,000 gallons per day. The two cones, each of 4500 gallons content, can together easily handle 50,000 gallons per day. The consumption of alum was decreased from 8 to 6 grains per gallon, and is still being gradually reduced.

The soda dose is introduced into the launder.

It was hoped that the floc could have been drawn off continuously from the spigot, but all attempts to maintain constant discharge of floc have failed, and a daily withdrawal has to be resorted to.

It is suggested that the cone type is the logical and most economical form of coagulating basin for all plants. Larger cones could, if necessary, be made with multiple conical or pyramidal bottoms to reduce depth. Obviously the plant would be made up of a series of cones which could be cut in and out to meet fluctuations, and would keep up efficiency while cleaning out.

Labour.—During the day one man attends to all operations. The night watchman looks in occasionally and adds chemicals if necessary.

The author desires to thank the Management of Apex (Trinidad) Oil-fields, Ltd., for permission to publish details of their plant, and wishes to acknowledge suggestions and criticisms received from Lt.-Col. H. C. B. Hickling, D.S.O., Mr. G. H. Scott, Mr. A. P. Till and the late Mr. P. James.

APPENDIX I.

Bacteriological Analysis.

A. Raw Water from River.
- (*a*) Colonies on agar = 176 per ml.
- (*b*) Presumptive *B. Coli* present in 0·1 ml.
- (*c*) Typical *B. Coli* in 0·1 ml.

*B. After Coagulation and Sedimentation.**
- (*a*) Colonies on agar = 84 per ml.
- (*b*) *B. Coli* absent from 50 ml. to 1 ml.

C. After Filtration.
- (*a*) Colonies on agar = 62 per ml.
- (*b*) *B. Coli* absent from 50 ml. to 1 ml.

Amongst the desiderata for a good potable water, *B. Coli* should be absent in 40 ml.

* Sedimentation of the floc.

APPENDIX II.

Typical Chemical Analyses of Raw Water.

Source.	John River.	Cunapo River.	Reservoir A.	Reservoir B.
pH	6·4	6·6	7·4	6·8
Before Filtration	Brown	Brown	Yellow : Milky	Yellow-brown
	Fair Turbidity	Fair Turbidity	Low Turbidity	Slight Turbidity
After Filtration	Clear Brownish	Clear Brownish	Clear Yellowish	Clear Almost Colourless
		Parts per million :—		
Sodium and Potassium ($Na' + K'$)	14	36	35	110
Calcium (Ca'')	5	3	7	7
Magnesium (Mg'')	4	2	6	5
Ferric Oxide and Alumina ($Fe_2O_3 + Al_2O_3$)	4	5	2	5
Carbonate (CO_3'')	—	—	—	—
Bicarbonate (HCO_3')	40	43	59	92
Chloride (Cl')	16	25	44	137
Sulphate (SO_4'')	4	23	7	9
Silica (SiO_2)	15	44	41	56
		Grains per gallon :—		
Alum Dose	6–7	12–20	4–8	6
Reaction	Good	Difficult	Ready	Ready

Bibliography.

[1] W. A. Taylor, Ph.D., "The A.B.C. of Hydrogen Ion Control." La Motte Chemical Products Company.
[2] C. R. Cox, *J. Amer. Water Works Assoc.*, 1934, **26**, 1587–1601.
[3] P. A. Morley Parker, "Control of Water," 1913 Edition, p. 564.
[4] Peterson and Barton, *Ind. Eng. Chem.*, 1928, **20**, 51.
[5] E. L. Bean, *J. New England Water Works Assoc.*, 1933, **47**, 273–279.
[6] Parker, p. 558, *et al.*
[7] Parker, p. 562.
[8] Memorandum on the Double Coagulation Process. Publication by Alfloc Limited.
[9] A. G. Nolte and W. A. Kramer, *J. Amer. Water Works' Assoc.*, 1933, **25**, 1263–1278.
[10] Marsden C. Smith, *ibid.*, 1933, **25**, 254–259.
[11] Parker, p. 561.
[12] M. Y. Kwaja, A.M.I.S.E., L.S.E., *J. Inst. Sanitary Eng.*, 1935, **39**, 43.

DISCUSSION.

Mr. I. McCallum said the paper was particularly interesting, as at the moment his company were working on a continuous process for treating water. They had used in the past the batch system of coagulation, which they had not found very satisfactory, and they were now adapting what apparatus they had to a continuous process.

It was evident from the figures which the author gave that the surface water in Palo Seco was of considerably poorer quality than the water found at Fyzabad. The author dosed with 6–8 grains of sulphate of alumina per gallon, whereas they had sometimes to use 20–30 grains before they got coagulation and decolorization of the water. Even then the results were

unsatisfactory owing to the tendency for floc to remain in suspension. This was due partly to the fine nature of the floc and also to the presence of bubbles which were enmeshed in the precipitate and prevented settling. The formation of these bubbles was attributed to the interaction of the coagulant with the sodium bicarbonate naturally present in the water.

The author made certain remarks about discoloration of water after it had been clarified. They had found the same difficulty in Palo Seco, and it had been his opinion that it was not due to the formation of iron–tannin compounds, but was the result of oxidation of the ferrous iron to ferric after the coagulation process, giving rise to a yellow tinge in the finished water. He had actually found that the use of an iron-free sulphate of alumina made no appreciable difference, and it seemed to him in any case that tannin, being of a complex organic nature, should be eliminated by the alum treatment.

The author mentioned that he did not consider the *p*H value during coagulation to be of any great importance. They had found that in the Jar Test taking a steady dose of alum and varying the alkali treatment there was in general an optimum quantity of alkali which gave better coagulation than a dosage on either side, and he thought it was a point which should always be watched, although on occasion the raw water can be insensitive to *p*H variation.

He was particularly impressed with the small dimensions of the plant described in the paper, taking into account the quantity of water which was handled, and he would ask the author whether he found any difficulty in settling the floc. It seemed that the whole design depended on the rates of flow for settlement of the floc mentioned in the paper, and that any variation in the properties of the floc such as were encountered at Palo Seco would entirely nullify the advantage of this type of plant. The floc, instead of settling, would pass over and deposit on the filter.

Another point of interest was with regard to corrosion. The author found that corrosion did not take place at *p*H 5·2 in his plant. At Palo Seco the water was invariably on the alkaline side, but still they got very appreciable rust formation in their water lines, even when the *p*H value was well over 8·0.

He could confirm the author's remarks about stirring of the water after dosage. He himself found that after the alum was added to the water it seemed to be very sensitive to the way it was handled during coagulation, and to ensure the efficiency of the process, stirring should be carried out. In addition, they had realized the necessity of isolating the dosed water until coagulation had reached completion, otherwise dilution took place and reduced the efficiency of the process.

With regard to the Jar Test, he would ask the author what correlation he found between his test and the actual plant dosages used. Personally he found the plant dosages were in excess of the quantities found in the test.

Mr. W. L. Rowland said he was reading a paper a few weeks ago on the purification of water which was criticized by Mr. Howard Humphreys, and he briefly summed up that it seemed quite fitting to anybody who had anything to do with water that the engineer and the chemist must work

together. He said that this had not been understood in the past, but there was no doubt it would have to be understood in the future. He thought from what the author had told them that night that they could all agree that the engineer and the chemist were one in that matter. He might also say that the Medical Department should be interested.

There was one question he would like to put to the author, that was, whether the light construction of the cement lining with the wire-netting reinforcement had suffered any damage through contraction or expansion from the clay sub-soil.

Dr. E. J. Sankeralli said he was entirely in agreement with what Mr. Rowland had said that no branch of science could be independent of another, and it made him realize more than he had before how much his own branch had to depend on the help received from the other professions.

The author had taught him a great deal that night, and he was especially grateful because at the moment it was something of great importance to them all. In his paper the author had standardized a method which could be adopted, perhaps at the minimum cost, by oil-fields and sugar estates.

In a part of the paper the author mentioned the difficulty in treating the Cunapo water, and attributed his difficulty to the possible hardness of the water, as the sulphate figure was higher in that water than in the others. The author might pardon him for the suggestion that perhaps if it was possible to treat the Cunapo water by the addition of quick lime he might be able to solve the difficulty. Houston suggested the addition of 1 or 2 parts per 50,000 parts.

From his own experience of similar controlled supplies, although the need for sterilization had never arisen at the plant described by the author, he felt that it would be safer to be provided with a means of applying chlorine in case of emergency.

They would pardon him if he struck a pessimistic note, but he recently had to deal with an epidemic, and it was his opinion that were it not for the fact that a chlorinating plant was available, they would have had much more difficulty in controlling the epidemic. He did not think that was an expensive item, and the Patterson type was used in several places.

The author said in his paper that he had not much experience in the use of ammonia after chlorine. It had been found that 0·25–0·5 per cent. of ammonia per million gallons would further the action of chlorine. The chemical reaction, as far as he could remember, was that a monochloramine was formed, and then later on dichloramine, and the point of importance was that this was not hindered by the presence of any organic matter, being continued over a period of several days, and the resultant water was tasteless. He believed, though he had no ground for making the assertion, it would be found that hydrogen-ion concentration would play a more important part in water analysis than at present. He thought they did not appreciate exactly the full extent of its importance.

He would like to ask the author if the cleansing of his filter was merely by a reversal of the flow, or if any attempt was made to use chemicals.

He would like to refer to one other point which did not come within the scope of that evening's paper, but which was nevertheless very important from his point of view. In certain places untreated surface water stored

in dams was being used as domestic supply. The difficulty he found was that usually at the end of the dry season the complaint was that the water was offensive. The author suggested the use of a swing arm. Mr. Rowland was a specialist in that line, and he perhaps would give more information, but the speaker thought if it were possible to attach to the dam draw-off a swing arm, reaching to a little below the water surface where aeration was most, they would do away with the difficulty of water having a bad taste and smell.

The proof of the pudding was in the eating, and the proof of the purification of water was in the drinking and in the chemical and bacteriological analyses. He would suggest that in addition to the routine bacteriological tests carried out as the chief means of control, arrangements should be made for a chemical analysis. He was certain that the work could be undertaken at the laboratories of the various companies, and it would be a preliminary indication of any change in the nature of the water.

A very interesting table from the engineering point of view had been added to the paper by the author and, if the latter would forgive him for making the suggestion, he would like to see a table of that kind kept as a routine measure of check. It should include any difference in the total and volatile solids, chlorine expressed as chlorides and nitrogen as nitrate. Nitrogen as nitrate in combination with chlorine would be most useful figures to have on file.

He had no further remarks to offer, and he thanked them for the opportunity of being present and listening to a most interesting address.

Dr. E. J. R. Macmahon said that he would like to mention that an analysis of their water was made each month and that, over a period of about five years, every analysis had been completely satisfactory.

Mr. G. H. Scott emphasized the advantages of the chemical dosage weir developed by the author, and considered it an ideal method for plants of small throughputs.

Mr. McCallum had pointed out that they could not settle their floc completely before the passage to the filter, and appeared to consider this was a serious disadvantage. Although this would tend to increase the water required for washing, many specialists definitely favour some of the floc passing to the filter, as it forms the so-called "Schmutzdecke" on the surface of the filter bed, and tends to reduce the bacterial count of the filtered water.

He considered that the coagulation effects produced by alum and ferrous sulphate were almost entirely a colloidal reaction, possibly helped to some degree by base exchange. The preponderant action was, however, due to adsorption factors.

In most turbid waters, the turbidity was in the form of colloidally dispersed particles with a negative charge. These would tend to be coagulated either by cations or by positively charged sols. It is well known that the higher the valency of the cation the greater will be the coagulation effect on a negative suspension. It was very significant, therefore, that aluminium, which has been proved to have such a rapid action, is trivalent.

If coagulation is considered as a fundamentally colloidal reaction, many of the findings of the author are fully vindicated.

Thus agitation or shaking of the water after the addition of the electrolyte, as recommended by the author, favours equal distribution of the electrolyte, which can then reduce the surface electric charge of the particles in the water and cause coalescence to commence.

Similarly the author's statement as to the requirement of a definite minimum addition of alum is again explainable by the fact that in order to ensure complete coalescence, sufficient electrolyte must be added to neutralize entirely the electrokinetic potential of the colloidally dispersed particles.

If crystalloids are present in true solution in the raw water, they may alter or modify the charge of the suspended particles, and he considered that this factor might explain the variations in minimum dosage requirements for varying sources of the raw water supply. He also considered that in some cases such variations in dosage requirements might be due to the presence of protective colloids such as tannates and humates which would retard the coagulation velocity.

The aluminium hydroxide is in the form of a positively charged sol, which on coagulation is converted into a gel. These gels tend to be peptized by acids, and he considered it possible that the presence of acids in the raw water might affect the formation of the floc.

Mr. A. H. Richard, in reply to Mr. McCallum about the difficulty in getting satisfactory settling of floc and having to use a very large dosage, said he would like to know the source of the water.

Mr. McCallum said they drew their water from various sources, but actually the water he was referring to contained a certain amount of contamination of well water and was highly alkaline. It was his opinion that that was largely the cause of the trouble. In addition, there was an excess of organic matter.

Mr. A. H. Richard : Was it derived from reservoirs or picked up from the stream ?

Mr. McCallum : Straight from the rivers.

Mr. A. H. Richard : His object in asking was because Mr. McCallum mentioned that most of the floc came to the surface and would not sink. On occasions they had difficulty of that sort with water derived from a more or less standing reservoir which was very slowly renewed. The floc, immediately after forming, floated instead of sinking. Flotation was due to large numbers of bubbles attached to the floc, the bubbles being either air or organically formed gaseous products. Eventually the bubbles would break and the floc would go down. They avoided putting such excess floc on the filters by having the outlet on a floating swing with the opening a few inches below the surface.

If the water was very alkaline, he would suggest consulting Peterson and Barton ;[4] they describe interesting experiments for such conditions in which they obtain improved results by acidifying the water.

He agreed that on occasion an optimum *p*H appeared to hold, but only on occasion ; at other times it did not help at all.

He had seen references in the literature that in many cases they have

had corrosion with alkaline waters up to *p*H 8·0. As a matter of fact, in the case cited by the author, corrosion may not have been due to the *p*H of 5·2.

With regard to correlation between the Jar Test and plant operation, a slightly smaller dose is obtainable in the plant than the Jar Test shows. There is nothing very much in it.

Mr. Rowland had inquired about damage to the lining. Their experience has been that there is no damage at all due to shrinkage of the sub-soil. There had been slight cracks within a few months after first construction, due to shrinkage of the grout, which have been filled up, and since then they had no further trouble.

Dr. Sankeralli suggested using lime for the Cunapo water. The author agreed that an improvement can be effected. As a matter of fact, he did use some lime at one time. He found the reaction easier, but still not anything as good as the other waters. The use of lime is a terrible nuisance, owing to its low solubility. It has to be constantly stirred, and for the plant and labour conditions with which the paper deals is out of the question.

As regards the use of ammonia with chlorine he had no experience, because he had never had occasion to disinfect. In the literature there was a great deal of doubt as to the benefits. Some authorities said that it was exceedingly good and reduced the dose of chlorine, and others found that it doubled it. One introduced ammonia at a certain point, either before or with chlorine and another somewhere else. There was nothing established about it.

There was one thing that seemed to be stressed in much of the literature, the importance of which he thought Dr. Sankeralli would realise more than he did. With ammonia, nitrites appeared in the filtered water, and he believed that was very beneficial to the growth of bacteria, and the process was, therefore, condemned by some authorities.

Filter cleaning was by wash water pure and simple, with agitation. If, of course, the filter was allowed to get foul, then the wash water could be dosed with chlorine or permanganate.

They used swing pipes in reservoirs, and Dr. Sankeralli was right in saying that if the water was taken from the bottom it was offensive. They kept their swing pipes somewhere off the bottom, but not necessarily at the top.

The author thanked Mr. Scott for his remarks.

CYCLIC CONSTITUENTS OF PETROLEUM CERESIN.

By JACOB MÜLLER and S. PILAT.*

WHILE investigating an analytical method for the determination of paraffin in asphalt,[1] it was observed that the paraffins precipitated from asphalt solely by means of solvents (*i.e.* without distillation) did not have a constitution corresponding to the formula C_nH_{2n+2}.[2] It was therefore found desirable to investigate the properties of these hydrocarbons which differed from normal paraffin, particularly in view of recent interest in ceresins obtained from petroleum residues by extraction processes.[3]

Without detailing the work of Zaloziecki,[4] Young,[5] Marcusson,[6] and Pictet [7] on normal and *iso*-paraffins, it should be pointed out that Pictet reported that he had obtained, from Boryslaw petroleum, a cyclic hydrocarbon identical with that isolated from beeswax. However, since the evidence of its cyclic constitution was insufficient, Marcusson considered that the material was a type of aliphatic hydrocarbon. As a result of further research, Marcusson came to the conclusion that cyclic compounds did not generally occur in ceresin. Recently, after the authors' experiments had been concluded, this question was reconsidered by Yannaquis.[8]

It was observed by the authors that paraffins which were precipitated from asphalt by solvent extraction processes had an elementary composition corresponding to the formula C_nH_{2n-2}. Although the iodine numbers of these products were about 6, the quantity of olefin hydrocarbons present could therefore scarcely exceed about 9 per cent., and hence the assumption that the substance consisted chiefly of hydrocarbons of cyclic constitution seems to be correct. In order to arrive at a definite decision on this point, the paraffin was purified by crystallization from pyridine, benzole and ether, in which the usual petroleum constituents are very easily soluble and in which, on the other hand, the high molecular undistilled paraffins are much less soluble. In this way pure products free from asphaltic resins and oil could be obtained.

PRECIPITATION AND PURIFICATION OF PETROLEUM PARAFFINS.

Fifteen hundred grams of asphalt obtained from a paraffinic Boryslaw crude oil, softening point 54° C. (Kraemer–Sarnow), were shaken for some time with 7500 g. of benzine (sp. gr. 0·649, b. pt. 30–50° C.). The clear solution was then separated from the asphaltenes, carbenes, carbon, etc., the benzine was distilled off and the reddish-brown oil remaining dissolved in 3 litres of warm pyridine (b. pt. 112–114° C. at 730 mm. Hg). In order to obtain the ceresin in an easily-filterable form, it was necessary to cool the pyridine solution slowly in a well-insulated vessel, otherwise gelatinous products are obtained which are difficult to filter. Filtration

* Petroleum Laboratory of the Technical Institute, Lemberg, Poland. Paper received April 11th, 1935. Translated from the German by Miss W. S. E. Clarke.

at 0° C. produced a mass of brown ceresin, which was recrystallized twice in the same manner, and 115 g. of a bright yellow ceresin, representing 7·67 per cent. of the asphalt, were obtained. The paraffin content of the asphalt, previously determined, amounted to 7·32 per cent., according to Marcusson, and to 8·63 per cent. by the pyridine method.

In order to remove coloured impurities, the ceresin was dissolved in 750 ml. of hot benzole and treated while hot with decolorizing charcoal.

Some elementary analyses were carried out at this stage, and the following results were obtained :—

0·1478 Substance . .	0·4671 CO_2.	0·1848 H_2O.	C, 86·17%.	H, 13·97%.
0·1574 Substance . .	0·4958 CO_2.	0·1978 H_2O.	C, 85·91%.	H, 14·07%.

$n_D^{65°} = 1·4620$. $n_D^{72°} = 1·4582$. $d_4^{65°} = 0·8143$.

Further refining was carried out by crystallization of the product from dry ether; large quantities of the solvent had to be used because of the extremely low rate of solution of this hydrocarbon. It was necessary to remove the solvent before cooling and crystallization. From 50 g. of the crude product analysed, 31 g. of refined material were obtained after two crystallizations from ether solution.

This operation was followed by crystallization from pure benzole, whereby the substance separated into four fractions.

Elementary Analyses.

The well-refined fractions were then accurately analysed. Each individual fraction, with the exception of the last, was burnt by Liebig's method in a long combustion furnace, and then elementary analyses were carried out on each fraction by Pregl's method. It was found that the results obtained by Liebig's method were more concordant, although the mean values obtained by both methods, with the exception of the first fraction, differed only very slightly.

The mean values recorded in Table I are those obtained by Liebig's combustion method.

The above classification of results shows that the fractions have a lower content of hydrogen than the corresponding hydrocarbons of the paraffin series. Moreover, the hydrogen content decreases from fraction to fraction with decrease in melting point, while, on the other hand, the refractive index, the specific gravity and the viscosity simultaneously increase. Since the iodine number corresponds to small quantities of hydrocarbons with double bonds, and oils have been completely removed by means of numerous crystallizations, it would appear reasonable to conclude that the difference in hydrogen content is due to the cyclic constitution of the solid hydrocarbons themselves.

Increase in specific gravity, refractive index and viscosity, with relatively small changes in molecular weight, suggest an even more marked cyclic constitution of the compounds from fraction to fraction. This can also be inferred from the slope of the temperature–viscosity curves. With decreasing hydrogen content of the fractions the viscosity curves become steeper, and even with the first fraction, which has the greatest hydrogen content, the viscosity decreases more quickly with increasing

Table I.
Ceresin from Petroleum Asphalt.

TABLE I.

Ceresin from Petroleum Asphalt.

Fraction.	Melting Point, °C.	d_4^{80}.	$\Delta d_4/1°$.	n_D^{80}.	$\Delta n_D/1°$.	C, %.	H, %.	Molecular Weight.	Formula.	Iodine Number.	Unsaturated Hydrocarbons, %.
1	75–80·5	0·7828	0·00065	1·4469	0·00038	85·47	14·49	700	$C_{49\cdot9}H_{100\cdot3} = C_nH_{2n+0\cdot3}$	1·4	3·8
2	60–60·5	0·8096	0·00062	1·4502	0·00038	85·64	14·37	758	$C_{54\cdot1}H_{108\cdot1} = C_nH_{2n-0\cdot1}$	2·3	6·9
3	50–58·4	0·8140	0·00058	1·4530	0·00040	85·70	14·16	775	$C_{54\cdot9}H_{105\cdot9} = C_nH_{2n-1\cdot7}$	4·1	6·3
4	49–56	0·8189	0·00063	1·4564	0·00035	85·93	13·97	695	$C_{49\cdot7}H_{93\cdot3} = C_nH_{2n-2\cdot1}$	3·9	5·4

TABLE II.

Ceresin from Ozokerite.

Fraction.	Melting Point, °C.	d_4^{80}.	$\Delta d_4/1°$.	n_D^{80}.	$\Delta n_D/1°$.	C, %.	H, %.	Molecular Weight.	Formula.	Iodine Number.	Unsaturated Hydrocarbons, %.
1	72·5–74·5	0·7867	0·00059	1·4400	0·00038	85·63	14·65	586	$C_{41\cdot8}H_{83\cdot3} = C_nH_{2n+1\cdot8}$	1·6	3·7
2	67–69·5	0·7788	0·00064	1·4398	0·00039	85·34	14·65	546	$C_{38\cdot8}H_{79\cdot4} = C_nH_{2n+1\cdot8}$	1·6	3·4
3	63·5–66	0·7836	0·00051	1·4405	0·00037	85·38	14·64	517	$C_{36\cdot8}H_{75\cdot1} = C_nH_{2n+1\cdot8}$	2·1	4·3

TABLE III.

Ceresin from Borjslaw Crude Oil Fractionated by Methane at Low Temperature.

Fraction.	Melting Point, °C.	d_4^{80}.	$\Delta d_4/1°$.	n_D^{80}.	$\Delta n_D/1°$.	C, %.	H, %.	Molecular Weight.	Formula.	Iodine Number.	Unsaturated Hydrocarbons, %.
1	51–55	0·7856	0·00061	1·4394	0·00036	85·43	14·69	483	$C_{34\cdot4}H_{79\cdot4} = C_nH_{2n+1\cdot8}$	1·6	3·0
2	42–50	0·7891	0·00059	1·4413	0·00038	85·36	14·51	467	$C_{33\cdot2}H_{77\cdot3} = C_nH_{2n+0\cdot8}$	1·2	2·2

Quantity.	CO_2.	H_2O.	C.	H.
Fraction 1.				
0·2012 g.	0·6299 g.	0·2597 g.	85·36%	14·46%
0·1477 g.	0·4631 g.	0·1914 g.	85·50%	14·51%
0·1779 g.	0·5580 g.	0·2304 g.	85·55%	14·50%
3·901 mg.	12·25 mg.	5·01 mg.	85·64%	14·37%
4·040 mg.	12·70 mg.	5·20 mg.	85·73%	14·40%
3·535 mg.	11·12 mg.	4·51 mg.	85·79%	14·28%
Fraction 2.				
0·1447 g.	0·4533 g.	0·1857 g.	85·44%	14·37%
0·1584 g.	0·4983 g.	0·2033 g.	85·80%	14·37%
0·1477 g.	0·4641 g.	0·1897 g.	85·69%	14·38%
3·791 mg.	11·91 mg.	4·84 mg.	85·68%	14·29%
3·694 mg.	11·61 mg.	4·69 mg.	85·72%	14·21%
3·284 mg.	10·30 mg.	4·23 mg.	85·54%	14·41%
Fraction 3.				
0·1509 g.	0·4742 g.	0·1907 g.	85·69%	14·15%
0·1421 g.	0·4469 g.	0·1795 g.	85·77%	14·14%
0·1733 g.	0·5442 g.	0·2198 g.	85·63%	14·20%
3·325 mg.	10·48 mg.	4·71 mg.	85·96%	14·03%
3·827 mg.	12·06 mg.	4·84 mg.	85·94%	14·15%
3·270 mg.	10·28 mg.	4·15 mg.	85·74%	14·20%
Fraction 4.				
0·1494 g.	0·4715 g.	0·1860 g.	86·07%	13·94%
0·1592 g.	0·5008 g.	0·1992 g.	85·79%	14·01%
3·709 mg.	11·71 mg.	4·65 mg.	86·11%	14·03%
3·368 mg.	10·61 mg.	4·20 mg.	85·92%	13·96%
3·085 mg.	9·72 mg.	3·84 mg.	85·93%	13·93%

temperature than with commercial paraffin or petroleum wax. From Fig. 1 these relations are easily observed with individual fractions.

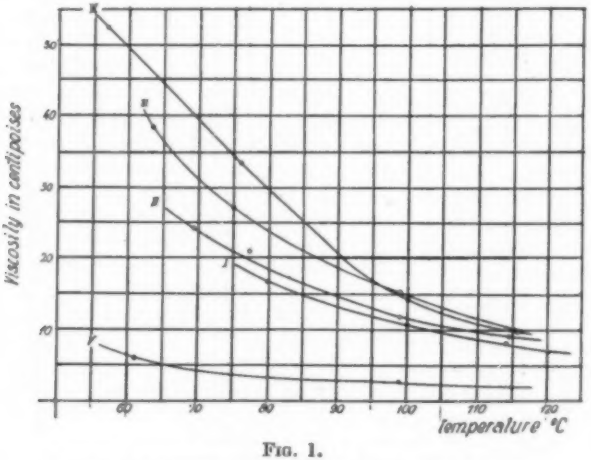

FIG. 1.

CERESIN FRACTIONS, I TO IV FROM ASPHALTS, V FROM COMMERCIAL PARAFFIN WAX.

These facts suggest that the solid hydrocarbons precipitated from petroleum asphalts are partly of cyclic constitution, and it would be interesting to establish whether this agrees with results from products from other waxes.

Boryslaw Ozokerite.

As already mentioned, Marcusson's view that ozokerite–ceresin consists only of aliphatic hydrocarbons has been disproved. However, according to his elementary analysis of the ceresin, somewhat lower hydrogen content was found than would be expected with paraffin, so that the possibility of obtaining cyclic hydrocarbons by fractional crystallization suggested itself.

Sixty grams of ozokerite (m. pt. 68·5° C.) were dissolved in 500 ml. of benzole, to which 60 g. of activated charcoal were added. After boiling for a short time, the mixture was filtered. The bright yellow-coloured

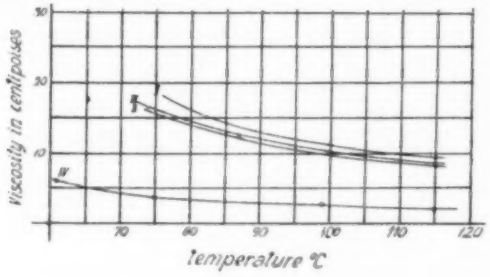

Fig. 2.

CERESIN FRACTIONS, I TO III FROM OZOKERITE, IV FROM COMMERCIAL PARAFFIN WAX.

material was next crystallized from 1200 ml. of pyridine, then from a mixture of 200 ml. pyridine and 600 ml. acetone, and finally from 1800 ml. of dry ether which had been heated under a reflux three times. Also, it was necessary to concentrate the ether solution by distillation to 500 ml. bulk before crystallization at 0° C. The crystalline material obtained from the ether solution was dissolved in 1300 ml. of warm benzole, and yielded, on cooling at room temperature, the first fraction. The second

Quantity.	CO_2	H_2O.	C.	H.
Fraction 1.				
0·1983 g.	0·6170 g.	0·2595 g.	84·85%	14·66%
0·1511 g.	0·4735 g.	0·1968 g.	85·45%	14·59%
Fraction 2.				
0·1662 g.	0·5205 g.	0·2174 g.	85·37%	14·65%
0·1635 g.	0·5115 g.	0·2140 g.	85·31%	14·66%
Fraction 3.				
0·1608 g.	0·5034 g.	0·2106 g.	85·35%	14·67%
0·1507 g.	0·4719 g.	0·1972 g.	85·39%	14·65%

fraction was obtained on concentrating the filtrate to 150 ml. After concentrating the resulting filtrate and adding 200 ml. of acetone, the third fraction was obtained. The fractions were maintained under a vacuum at 100° C. to constant weight and then analysed.

The above analyses, in addition to the results given in Table II and the relevant viscosity curves, signify that none of the fractions investigated contained cyclic hydrocarbons. Marcusson's view regarding the aliphatic nature of ozokerite hydrocarbons is thus fully confirmed by the above experiment.

Ceresin from Paraffinic Crude Oil Fractionated by Methane at Low Temperature.

Methane was passed at low temperatures into Boryslaw crude oil in order to remove the volatile material, a vacuum being applied to assist evaporation. Asphalts and resins were precipitated from the residue by saturation with natural gas under pressure,[9] and 200 g. of the asphalt-free product were mixed with 500 ml. of warm alcohol and the ceresin was

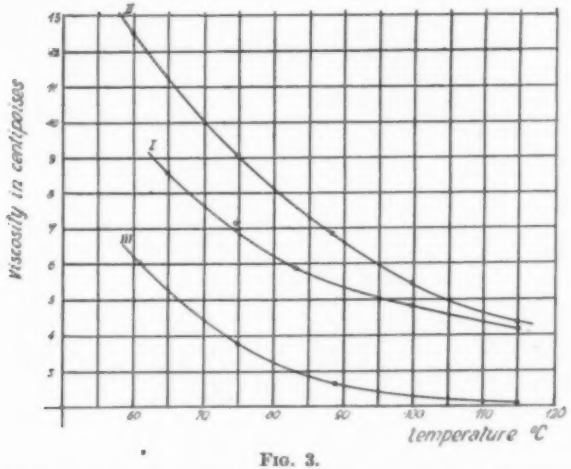

Fig. 3.

Ceresin fractions, I and II from Boryslaw crude petroleum, III from commercial paraffin wax.

precipitated at room temperature. The precipitate was recrystallized twice from 1000 ml. of pyridine alcohol and then from the same quantity of acetone benzole. The refined product obtained was dissolved in 500 ml. of dry ether, cooled to 0° C. and fraction 1 obtained. The ether was evaporated from the filtrate and the remaining material was next crystallized from acetone benzole, then twice from alcohol ether; by cooling and filtration, fraction 2 was obtained. Analytical results are recorded in Table III, and these show that the first fraction contains aliphatic hydrocarbons, whilst the second fraction is composed of a mixture of paraffinic and cyclic hydrocarbons, the latter constituting the major portion.

Quantity.	CO_2.	H_2O.	C.	H.
Fraction 1.				
0·1988 g.	0·6222 g.	0·2599 g.	85·36%	14·64%
0·1547 g.	0·4852 g.	0·2036 g.	85·52%	14·76%
Fraction 2.				
0·2026 g.	0·6344 g.	0·2625 g.	85·39%	14·51%
0·1865 g.	0·5833 g.	0·2413 g.	85·30%	14·49%
0·1499 g.	0·4692 g.	0·1945 g.	85·36%	14·53%

Very little can be deduced at present with regard to the structure of the cyclic constituents. Of the two explanations dealt with, the first originated from the assumption of the presence in the compounds described of 5- or 6-membered rings as well as longer side-chains, whilst the second assumption was of the presence of larger rings from numerous methylene groups. As is well known, Ruzicka and his collaborators [10] have prepared and described recently numerous hydrocarbons of this type.

TABLE IV.

Naphthene Hydrocarbons.

Hydrocarbon.	d_4.	d_4^{20}.*	n_D.	n_D^{20}.*
$C_{17}H_{34}$ Dipropyl*iso*butyl*cyclo*hexylmethane[11] .	0·8841 at 19° C.	0·806	1·4658 at 23° C.	1·443
$C_{18}H_{36}$ Methyldi*iso*amyl*cyclo*hexylmethane[12] .	0·8440 at 20·5° C.	0·806	1·4666 at 20° C.	1·443
$C_{19}H_{38}$ Ethyldi*iso*amyl*cyclo*hexylmethane[11] .	0·8681 at 20·5° C.	0·830	1·4789 at 20° C.	1·455
$C_{20}H_{40}$ Propyldi*iso*amyl*cyclo*hexylmethane[11] .	0·8421 at 20·5° C.	0·804	1·4646 at 20° C.	1·441
$C_{20}H_{40}$ 1-*iso*Hexyl-4-/αε-dimethyl-*n*-hexyl*cyclo*hexane[12]	0·8331 at 20° C.	0·795	1·4600	1·436
$C_{21}H_{42}$ *iso*Butyldi*iso*amyl*cyclo*hexylmethane[11]	0·8797 at 20·5° C.	0·842	1·4905 at 20° C.	1·466
$C_{17}H_{32}$ αε-Di*cyclo*hexylpentane[13] . . .	0·8719 at 21° C.	0·834	1·479 at 21° C.	1·455
$C_{17}H_{32}$ β-Ethyl-αγ-di*cyclo*hexylpentane[13] .	0·8846	0·847	1·489 at 21° C.	1·465
$C_{26}H_{52}$ 1 : 10-*bis*-1 : 1 : 3-trimethyl*cyclo*hexyl-(2)-3 : 8-dimethyldecane[14] . .	0·8860 at 17·3° C.	0·846	1·48583 at 17·3° C.	1·461
$C_{24}H_{46}$ Naphthene from Dossor Crude Oil[15] .	0·877 at 15° C.	0·836	1·4813 at 15° C.	1·455
$C_{21}H_{40}$ Naphthene from Grozni Crude Oil[15] .	0·876 at 15° C.	0·835	1·5075 at 15° C.	1·481
$C_{23}H_{42}$ Naphthene from Kaluga Crude Oil[15] .	0·898 at 15° C.	0·857	1·5177 at 15° C.	1·492

* Calculated against $\Delta d_4/1° = 0·00063$ and $\Delta n_D/1° = 0·0004$.

The lower coefficients of refraction and low specific gravities of the components described do not favour the first assumption. It is clearly evident from Tables IV and V that naphthenes corresponding to the authors' hydrocarbons would have a much higher molecular weight, and consequently still higher values for n_D.

TABLE V.

Aliphatic Hydrocarbons.

Hydrocarbon.	Melting Point, °C.	d_4.	D_4^{80}.*	n_D.	n_D^{80}.*
$C_{29}H_{60}$ *n*-Nonacosane[16] . . .	61·5–63·5	0·7798 at 64° C.	0·770	1·43061 at 80° C.	1·43061
$C_{32}H_{76}$ *n*-Dotriacontane[17] . .	70·5	0·7798 at 70° C.	0·773	1·4334 at 72° C.	1·4302
$C_{37}H_{76}$ *n*-Heptatriacontane[18] . .	77·4	0·7682 at 100° C.	0·791	1·4328 at 90° C.	1·4368
$C_{37}H_{76}$ 18-Ethylpentatriacontane[18].	39–40	0·773 at 100° C.	0·786	1·4348 at 90° C.	1·4388
$C_{38}H_{78}$ *n*-Octatriacontane[19] . . .	79·2–79·4	0·7688 at 100° C.	0·781	1·4326 at 90° C.	1·4366
$C_{39}H_{78}$ 18-*n*-Propylpentatriacontane[18]	64–65	0·781 at 100° C.	0·794	1·4376 at 90° C.	1·4416

* Calculated against $\Delta d_4/1° = 0·00063$ and $\Delta n_D/1° = 0·0004$.

From this fact, and also on account of the similarity of the properties of larger rings which, according to Ruzicka, could be considered as double chains, such compounds occupy a medium position between aliphatic and naphthenic hydrocarbons, and it would appear possible that ceresins precipitated from asphalts consist chiefly of polymethylene rings.

References.

1 *Asphalt u. Teer*, 1932, **32**, 708.
2 *Nature*, 1934, **134**, 459.
3 *J.I.P.T.*, 1935, **21**, 2.
4 *Z. angew. Chem.*, 1888, **1**, 261, 318.
5 *J.C.S.*, 1899, **15**, 22.
6 *Chem. Z.*, 1915, **39**, 613.
7 *Ber.*, 1915, **48**, 930.
8 *Ann. des Comb. Liq.*, 1934, **2**, 295.
9 *Przem. Chem.*, 1934, **18**, 376; *J.I.P.T.*, 1935, **21**, 60A.
10 *Helv. Chim. Acta*, 1934, **17**, 78–87, and previous works by the same authors.
11 *J. für prakt. Chem.*, **92** (2), 47–48.
12 *Ber.*, 1914, **47**, 2077.
13 *Compt. rend.*, **156**, 1431–1434, 1952–1953; *Ann. Chim. Phys.*, **4** (9), 306–308.
14 *Helv. Chim. Acta*, 1932, **15**, 878–906.
15 *Erdöl. u. Teer*, **9**, 220.
16 *Ber.*, 1907, **40**, 4783; 1918, **52**, 1040.
17 *Chem. Zentr.*, 1913, **1**, 2108.
18 M. Pogacnik, "Iso-structure of Ceresin Hydrocarbons. Discussion."

THE COKING OF PETROLEUM RESIDUES.*

By D. Glynn Jones, M.Sc., M.Am.Assoc.Pet.Geol.
(Associate Member).

SYNOPSIS.

The present paper outlines the evolution of a novel method of coking petroleum residues. The application of the scheme to a particular heavy residue is discussed, together with an account of the experimental work entailed. Brief descriptions are also given of some commercial coking systems.

Apart from the question of lubricating oils, the modern trend of refining is the production of increasing quantities of motor fuels from a given quantity of crude oil. In this case the term motor fuel comprises fuel for internal-combustion engines and fuel for compression-ignition engines. This increase has been brought about in the past mainly by the employment of cracking. Hydrogenation, too, is now playing its part, but this is a process for larger companies rather than for the small refinery. It is on account of the desire for more motor fuel that the investigations related herein were undertaken, resulting in the installation of a coking plant of rather novel design.

The basic crude petroleum available is Comodoro Rivadavia crude, the character and treatment of which have been described by the Author in an earlier paper.[1] The crude itself contains merely a trace of gasoline on entering the refinery, but by a combination of low-pressure cracking and high-pressure cracking, some 27 per cent. of gasoline by volume is eventually obtained. The residue is a fuel oil of characteristics :—

Specific gravity at 15° C.	0·980
Viscosity Saybolt Furol at 50° C.	350 sec. (Max.)
Sediment	0·5 per cent.
Hard asphalt	11·0 per cent.
Sulphur	0·19 per cent.
Calorific value	18,500 B.Th.U.
Pour point	40° F.
Flash point (Pensky Marten)	184° F.

All intermediate products such as gas oil and kerosine are at present cracked in the Cross cracking plants.

A simple way of increasing the yield of motor fuel is by coking residues. In this operation a small quantity of gasoline would be produced directly, together with a gas oil suitable for cracking, probably a useful diesel oil, and a quantity of gas and coke. The refinery flow-sheet presented various residues which could be conveniently coked, influencing adversely only the production of fuel oil, a product fetching a low price, and the loss of which would be more than counterbalanced by the increased yield of motor spirit.

A series of preliminary experiments was performed in the laboratory,

* Paper received April 22nd, 1935.

testing the value of each possible residue. A small cylindrical cast-iron coking still of capacity 500 ml. was made having a tightly fitting lid containing an aperture for a thermometer, the vapour outlet being a bent copper tube fitted with a water-jacket. The end of the condenser tube fitted into a glass receiving vessel. This in turn was connected to a gas holder maintained under atmospheric pressure (as indicated by a mercury manometer) by means of a reservoir suspended on a frictionless pulley, the discharge level of the water being automatically adjusted by a counterbalancing device working in a glass tank. The whole apparatus was completely gas-tight. A charge of oil was carefully weighed out into the coking vessel and the temperature gradually brought up to 500° C. and maintained until no further evolution of gas took place. When cold, the coke produced was weighed, the distillate measured, and the volume and density of gas formed were ascertained. The distillate was submitted to an A.S.T.M. distillation in order to determine the approximate percentage of gasoline (boiling up to 200° C.) present. Some typical results follow :—

Charging Stock.	Coke.	Distillate.					Gas.		
	Per cent. by weight.	Per cent. by weight.	Sp. Gr.	I.B.P. ° C.	Per cent. off at 200° C.	Per cent. off at 300° C.	M³/ton charge.	Sp. Gr. (air=1).	Per cent. by weight.
Topped crude. Vis. 350 sec.	15	80	0·878	68	11	32	40	1·0	5·2
Kellogg residue. Vis. 2000 sec.	22	70	0·881	87	10	25	70	1·0	8·0
Cross residue. Vis. 20 sec.	11	85	0·901	132	2	11	30	1·0	4·0
A steam-blown asphalt. Soft. Pt. 54° C.	36	60	0·978	78	17	25	110	1·0	14·3

Note.—All viscosities are Saybolt Furol at 50° C.

The results obtained above were confirmed by a large-scale test in which some 10 kilos. of residue were coked at a time, temperature conditions being similar in each case. This method produced sufficient distillate for a rough fractionation to be effected, and at the same time yielded enough coke for analytical determinations.

From many points of view the most favourable raw material for coking is a residue from which no further gas oil or motor spirit can be produced by ordinary means. These conditions are fulfilled in part by Kellogg residue, but better still by a reduced Kellogg residue, which is in reality an asphalt. The reduction of the residue to an asphalt can be brought about either by vacuum distillation or by a steam distillation. An oxidized asphalt in this case would not be convenient, as, apart from other considerations, it involves an extra process for its elaboration. From this stage, therefore, experiments were concentrated on Kellogg residue.

This material is a product of cracking topped Comodoro crude in two Kellogg low-pressure cracking plants or viscosity breakers. In these plants the crude is submitted to a maximum temperature of 450 to 460° C., while being held under a pressure of 250 lbs. per square inch. Pressure is released at the outlet from the furnace tubes, and the hot oil is injected into an evaporator, from the bottom of which the residue is drawn off, usually for blending with Cross cracking plant residue to make a saleable fuel oil.

By its passage through the furnace, the viscosity of the charging stock is reduced from 350 sec. Saybolt Furol at 50° C. to 30 sec. In the fractionating tower which follows the evaporator, gas oil and crude motor spirit are separated. The average yields obtained from the plant based on volume of feed are :—

Crude motor spirit (sp. gr. 0·750, E.P. 200° C.)	7·5 per cent.
Gas oil (sp. gr. 0·890)	40·3 „
Heavy residue (vis. 2000 sec.)	48·2 „
Loss as gas, etc.	4·0 „

The distillation of Kellogg residue under atmospheric pressure is accompanied by cracking, but in subjecting it to a distillation under an absolute pressure of 5 mm. of mercury, some 40 per cent. of distillate is obtained, the still head temperature rising to 310° C. The analysis of this distillate is :—

Specific gravity at 15° C.	0·935
Initial boiling point	190° C.
Recovery at 200° C.	0·5 per cent.
„ at 300° C.	4·0 „
„ at 350° C.	11·0 „
„ at 400° C.	70·0 „
Viscosity Saybolt Universal at 38° C.	453 sec.
„ „ „ at 50° C.	196 „
Conradson carbon value	0·58 per cent.

The 60 per cent. residue (asphalt) from the vacuum distillation possesses the properties :—

Softening point (Ring and Ball)	58° C.
Penetration 25° C., 100 g., 5 min.	60
Ductility 25° C., 5 cm./min.	2 cm.
Solubility in carbon disulphide	96 per cent.
Asphaltenes (hard asphalt)	25 „
Asphaltum (soft asphalt)	67 „

Preliminary experiments indicated that from each 100 tons of this product charged to a coking system, some 12 M^3 of crude gasoline, 30 M^3 of gas oil, 30 M^3 of heavy distillate, and 21 tons of coke would be produced. These results were sufficiently satisfactory to justify the installation of coking ovens. The gas oil would be cracked in the Cross cracking plants, the heavy distillate re-circulated to the Kellogg plants, and the gasoline cut refluxed to the Cross unit bubble towers and refined as far as possible in the normal way, together with the usual production of gasoline.[1]

Methods of Coking Petroleum Residues.

Numerous methods of producing coke and light distillates from petroleum residues have been devised. One of the earliest, and probably still the most widely adopted, is the use of a fire-still, either of horizontal type or of the vertical "cheese box" pattern. These stills are usually of $\frac{1}{2}$ to $\frac{5}{8}$ in. steel plates, and a fairly common size is 14 ft. × 40 ft. The stills are fitted with the usual vapour outlets, charging connections, manholes, safety-valves, etc. At one time it was common practice to build them in pairs, arranged for side firing, but end-fired stills have largely superseded this type, and are arranged in batteries of six or more. A typical installation is described by Staley,[2] in which he gives details of the "Atlantic"

process. The charge, which may be residuum from asphalt-base crudes, slop cuts, wax tailings, and cracking units, is preheated to 385° C. in a pipe still and charged to the coking stills. These are arranged in batteries of sixteen, two stills charging simultaneously, each being filled with some 700 barrels. The temperature is maintained at 340° C. during the charging, which takes about 2¾ hours, after which it is gradually increased to 425° C. during a 10-hour period. The stills are kept at this temperature for a further 15 hours or so, when the coking is complete. One hour is then allowed to relieve pressure, followed by 2 hours of steam injection to drive out all vapours remaining. The removal of the coke is facilitated by the introduction of twenty steel frames into the still before charging. They are all linked together, and coke forms in and around them to a depth of several feet. After the head is removed from the still, a cable is attached to the coke pans and they are pulled out by means of a winch. The coke remaining in the still is removed by labourers. The coke is cooled by a water-spray, loaded into wagons and removed to storage.

It should be noted that this process differs from the majority of simple coking plants in that the head of the still is removable. Normally the still-head is merely provided with a manhole through which coke is removed by labourers.

In the above description of the "Atlantic" process, the total cycle time is not given, but allowing 2 hours for cleaning out and preparing for the next operation, some 33 hours are required for each charge, *i.e.* to coke 700 barrels, leaving a coke residue of 15 per cent.

A typical operational cycle for a simple installation coking 150 barrels per still of heavy fuel oil (specific gravity 0·940) entering at a temperature of 90° C. follows :—

From firing still to beginning of distillation	7 hours
From beginning of distillation to fires out	4 ,,
Cooling still	2 ,,
Injection of steam	1 hour.
Cooling by induced draught through manholes, etc.	2 hours.
Cleaning and preparing for next run	5 ,,
Total cycle time	21 hours.

In this case distillation is continued until the still bottom is a bright red.

Stills of the type described above suffer from many disadvantages, among which may be mentioned: severe local overheating, leading to burning of the steel and need for frequent replacement of still bottoms; difficulty in producing good-quality coke, in that shell stills do not turn out a dense, hard coke; furthermore, shell stills have a rather high attendant fire risk.

The Knowles process[2,3] represents an attempt to overcome these disadvantages. In this system a preheated charge of heavy residue is destructively distilled in retorts or ovens with a refractory floor and an arched roof having appropriate inlet and outlet connections. The preheater commonly used for this process is a pipe still, in which the heavy oil circulates at a velocity sufficiently high to obviate coke deposition in the furnace tubes. In this way the charge is raised to a temperature of

450° C. The ovens proper are structures 30 ft. long by 10 ft. wide, having a sprung arch 5 ft. high at its centre. The oven arch tile has a low coefficient of expansion, and expansion joints are provided in the walls between the ovens. The oven floor is of refractory tile (carborundum has given very good results), and below the floor, at each end of the oven, are two horizontal rows of gas burners, each row being fitted to separate headers, so as to allow of adequate control of firing. The oven doors, one at each end, consist of a steel frame lined with refractory tile, suitably sealed when closed to prevent ingress of air to the ovens. A mechanism is provided for raising the oven doors for discharging the coke, an operation performed by a ram. The entire ram assembly is mounted on wheels traversing two rails running parallel to the line of the oven ends. A single vapour off-take is set into the top of each arch, midway between oven ends. This connects to a vapour header, and thence to the fractionating tower and condensing equipment. During the coking operation the ovens are held under a vacuum of approximately 0·10 in. water.

The mode of working the Knowles ovens is as follows:—

The preheated charging stock is sprayed on the oven floor during a period of approximately 2½ hours, during which time the oven temperature is dropped to 425° C. The charge is then dried out, the oven temperature gradually rising to 560° C., complete dryness being indicated by this temperature having been reached at the bottom of the vapour off-take. It is found that best results are obtained by allowing a bed of coke 7 to 8 in. in thickness to build up. When the coke is dry, the doors are raised and the ram is operated, the quenching car being in position at the other extremity of the oven. The quenching car goes immediately to the quenching station, where the hot coke is deluged with water. From the quenching station coke proceeds to the screening plant for any further treatment which may be necessary to render it marketable.

Other methods of coking heavy residue have been patented, but details of their practical applications are not available. Among these methods may be mentioned the following:—

In two patents coking is effected by injection into a chamber lined with a catalyst [4] or by injection into a heating zone constructed of a metal alloy.[5] The heated oil is injected together with steam in both cases. The catalyst used in the first patent consists of 14 parts silica, 9 parts sodium silicate, 4 parts alumina, 2 parts zinc oxide, a trace of magnesite and a trace of lime. The alloy used in the second patent is a 90 per cent. nickel chromium alloy containing small portions of silica, zinc, aluminium and iron. Iron oxide is also injected in this process, in order to desulphurize the charging stock.

Another patent [6] covers the manufacture of coke by spraying fluid bituminous material into a chamber, together with a continuous supply of gas, such as steam. The operation is so controlled that the material is converted into a partly coked, but still plastic, product while falling through free space in the chamber.

Another process for converting heavy oil into distillates and coke consists [7] in spraying the heated oil into a chamber where falling droplets of oil came into contact with ascending steam.

In a further patent, low-pressure reduction to coke of residuum from

cracking operations is brought about by the use of heated hydrocarbon vapours produced in the cracking plant.[8]

All the processes mentioned above suffer from the disadvantage of being discontinuous. When the chamber or oven contains a certain limited amount of coke, operation has to be suspended for this to be removed. The most satisfactory method of coking petroleum residue would be one in which the operation is continuous—that is, one in which the products of coking would be continuously removed without the interruption of the coking process, with the attendant loss of heat and time and the consequent reduction of throughput. It is with a process of this type that it is now proposed to deal, culminating in the construction of an actual working plant, for which results are given.

While it is not possible to follow out the evolution of the continuous process in detail, it is interesting to note the following steps in its development:—

In 1915 an English patent[9] was taken out by R. S. Richards and The Smokeless Fuel Syndicate, in which this idea was applied to the destructive distillation of coal. The invention comprised upper and lower longitudinal chambers connected at either end by external chambers which housed a wheel and drum adapted to carry a chain conveyor. The chain conveyor consisted of overlapping trough-like sections which passed through the upper and lower chambers, combustion chambers being disposed between the two. Means were incorporated for filling the conveyor at one end and discharging the conveyor at the other end. It should be noted that this invention had specific reference to the production of smokeless fuel and by-products, from solid carbonaceous material, and formed an improvement to the apparatus described in a patent granted to R. S. Richards and R. W. Pringle in 1909.[10]

A somewhat similar plant was patented in 1929 by J. G. Grondel and C. C. Carlson,[11] the trough-like conveyor being replaced by an endless chain grate composed of parallel sets of links, the chain being driven by a drum having teeth provided on its circumference corresponding to the openings in the grate. The apparatus is suitable for the dry distillation of coarse and fine material, coarse material being first fed on to the chain, thereby preventing fine material from dropping through.

The final patent to be mentioned is that of W. Möhring,[12] which forms the basis of the coking plant recently put into operation. This may be described as an apparatus for coking distillation while the charge passes in a chain arrangement of containers through a furnace heated on all sides. This process, however, is not strictly continuous, in that the filled containers are introduced intermittently into the furnace, the outlets of the chamber being closed by two sealing members incorporated in the chain of containers for this purpose. Distillation of the contents once completed, the containers are withdrawn from the furnace, their place being taken by other filled containers.

Tests on the Experimental Plant.

Having decided on the installation of a coking plant incorporating the last patent, various points arose as to the best type of coking chamber to

employ, the best disposition of the container with respect to the floor and sides of the chamber, and the best operating conditions in general. In order to come to a decision, an investigation was carried out on two experimental coking plants of the same general design (see Fig. 1).

The smaller experimental plant was fitted at first with a refractory brick coking chamber; this was later replaced by one of cast iron. The chamber accommodated five containers of cast iron, each holding 20 litres of residue. The burners were arranged below the floor of the chamber, and combustion gases circulated around the sides of the chamber and over the top before passing out to the smoke stack.

The large experimental plant was similar to this, except that the coking chamber was of refractory brick accommodating four containers of cast iron each holding 250 litres of residue.

The general operation of the plant was as follows:—

The receptacles for the residue were rectangular cast-iron buckets,

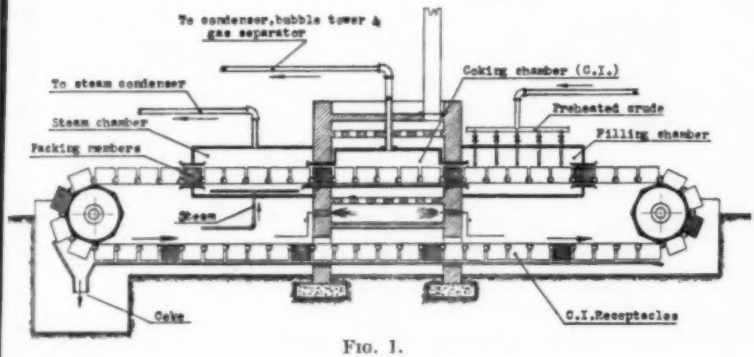

FIG. 1.

DIAGRAM OF EXPERIMENTAL PLANT.

arranged in the form of a train, passing around two driving-wheels at either end of the plant. At intervals corresponding to the length of the coking chamber were packing members which effectively sealed up the ends of the filling chamber, coking chamber and cooling chamber, respectively. While the contents of one set of containers was being distilled in the coking chamber, another set was being filled with preheated fuel oil at one end, and the set which had just been moved out of the chamber was cooling in an atmosphere of steam in an extension of the furnace specially adapted for this purpose. On the next move of the system, the cooled containers would be cleaned (manually) of their coke. Eventually, by passing down underneath the furnace, the cycle would be repeated. A set of buckets would be filled with preheated crude, coked in the chamber, cooled in an atmosphere of steam, emptied of coke and passed back inverted, in the reverse direction, until they once more reached the filling chamber.

The vapours from the distillation passed up a vapour outlet in the top of the coking chamber, through a condensing system to a gas separator and run-down tanks. Gas was measured by a simple orifice meter and liquid distillate gauged by dipping the tanks. It should be mentioned

that a vacuum of 10 mm. of water was held in the system by means of a steam ejector or a fan extractor.

The behaviour of the charging stock under coking conditions was already known from laboratory experiments, and the study of the experimental installation was therefore undertaken mainly in order to work out the heat duty on the system, the heat transfer system involved, and the influence of these factors on the design of a full-scale commercial coking plant.

Some six thermocouples or thermometers were employed in the oven, coking chamber and vapour outlet, their position being depicted in Fig. 2.

In the absence of sufficient recording instruments, temperatures were noted every five minutes over a number of runs, the figures finally used

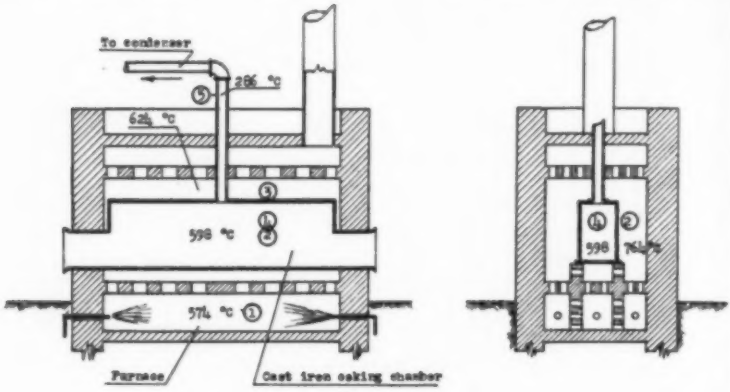

FIG. 2.

DIAGRAM TO SHOW POSITION OF THERMOCOUPLES (INDICATED BY CIRCLES).

in the calculations being averages. The positions of the thermocouples were :—

(1) In the furnace combustion space below the coking chamber. (574° C.)
(2) In the furnace combustion space halfway up side of chamber. (764° C.)
(3) In the furnace combustion space above the chamber. (624° C.)
(4) In the coking chamber itself. (598° C.)
(5) At vapour outlet. (286° C.)

The figures in parentheses indicate the average temperatures during a cycle.

HEAT DUTY ON COKING CHAMBER.

Charge to Chamber.

Coking chamber is of cast iron. (2090 mm. × 600 mm. × 370 mm.)
5 cast-iron buckets of 60 kilos each.
100 litres of fuel oil at 130° C. (270° F.), (sp. gr. 0·941 at 15° C.).
Weight of fuel oil = 87 kilos.

Products.

Crude distillate, 75 per cent. by weight.
Coke, 6 per cent. by weight.
Loss (gas and entrained light products), 19 per cent. by weight.

Total coking time.

100 minutes (average).

Temperatures.

Average temperature in chamber, 600° C. (1100° F.).
Average heat gradient between chamber and furnace, 56° C. (100° F.).
Assume all oil distilled off at 400° C. (750° F.).
Coke and buckets then raised to 600° C. (1100° F.).
Buckets and fuel oil enter chamber at 130° C. (270° F.).

Total heat requirement.

	B.Th.U.
(*a*) Heat to buckets. (5 × 60 × 2·2 × 830 × 0·1)	55,000
(*b*) Heat to oil. (87 × 2·2 × 480 × 0·64)	59,000
(*c*) Heat to raise temperature of coke. (5 × 2·2 × 350 × 0·4)	1,500
(*d*) Heat to vaporize 94 per cent. of fuel oil. (82 × 2·2 × 60)	10,800
(*e*) Heat to crack. (87 × 2·2 × 100)	19,000
Total heat required	145,300

This does not allow for radiation losses, etc., and is merely a very approximate figure. The average hourly duty on the chamber is therefore 87,000 B.Th.U.

Approximate coefficient of heat transfer through coking chamber of cast iron,

$$K = \frac{145{,}300 \times 60}{100 \times 45 \times 100} = 19{\cdot}4 \text{ B.Th.U./sq. ft./1° F./hr.}$$

In the same way, allowing for a coking time of 120 minutes as against 100 minutes for a cast-iron chamber, the coefficient of heat transfer through a chamber of refractory bricks was calculated to be 2·9 B.Th.U./sq. ft./1° F./hr.

The coefficient of heat transfer was also calculated (from experimental results) for a coking chamber (dimensions 13·5 ft. × 2·0 ft × 4·3 ft.) of refractory bricks. These calculations gave the result of 3·5 B.Th.U./sq. ft./1° F./hr. An average figure of 3·2 can therefore be assumed for a refractory brick chamber, as against 19·4 for a cast-iron chamber.

The conclusion reached, therefore, from these results is that from a point of view of heat transfer a cast-iron chamber is preferable to one of refractory brick. In other respects, too, it is superior in that the construction of the oven is greatly simplified. Cast iron suffers, however, from certain inherent defects, such as the development of brittleness on

exposure to high temperatures, and so the commercial plant was constructed with a coking chamber of heat-resisting manganese steel.

The next point to be solved was the best method of disposition of the buckets within the coking chamber. This question is intimately connected with the mode of transfer of heat inside the chamber—that is, whether heat is transferred to the buckets and their contents by conduction, convection or radiation. In the experimental plant, the containers were supported on two narrow runners (10 mm. wide × 5 mm. high) cast integrally with the chamber. The clearance between the sides of the containers and the walls was 15 mm. each side.

The possible methods of heat transference are therefore :—

(1) *Conduction* through the metal–metal contact at the bottom of the chamber and through gases at sides and top of chamber.
(2) *Convection* through gases at bottom, sides and top.
(3) *Radiation* from all sides of the coking chamber to the enclosed approximately rectangular mass of the containers.

In the case of the experimental plant, the area of metal–metal contact was very small, being limited to the two parallel runners at the bottom of the chamber. Some conduction could also take place through the gas spaces at the sides, bottom and top, but the coefficient of conductivity of heat through gases is so small that this accounts for an insignificant amount of the heat input. Convection is practically limited to the gases and vapours above the coking residue, but as there is a vacuum (10 mm. water) being pulled on the vapour outlet, downward convection currents are reduced to a minimum. It therefore appears that radiation is mainly responsible for the transference of heat. Confirmation of this was obtained by an approximate calculation of the theoretical heat transferred by radiation from the sides of the chamber to the containers and their contents.

Calculation of Heat Transfer to the Buckets by Radiation.

Average temperature of chamber, 600° C. (1100° F.).
Mean temperature of buckets and their contents, 370° C. (700° F.).
Area of absorbing surface, taking total superficial area as that of a solid block of metal of similar dimensions to the train of buckets = 20 sq. ft.

whence $$Q = 0{\cdot}172 \times A \times P_e \left[\left(\frac{T_1}{100}\right)^4 - \left(\frac{T_2}{100}\right)^4\right]$$

where P_e = relative blackness of enclosed body (assume 0·7).
A = superficial area of enclosed body.
T_1 and T_2 = absolute temperatures (° Rankine) of hot and cold bodies, respectively.
Q = Total heat transferred in B.Th.U. per hour.

whence $$Q = 0{\cdot}172 \times 20 \times 0{\cdot}7 \left[\left(\frac{1560}{100}\right)^4 - \left(\frac{1160}{100}\right)^4\right]$$
$$= 102{,}000 \text{ B.Th.U.}$$

There are various unknown and complicating factors which cannot be taken into the calculations, such as

(1) Some of the heat received by the oil is by direct radiation;
(2) Some is by conduction through the sides of the buckets;
(3) The volume of the oil is constantly diminishing;
(4) The coefficients of relative blackness of the component elements are unknown, 0·7 merely being used as an approximation.

Hence, it is not claimed that the figure of 102,000 B.Th.U. is very accurate.

The calculated heat duty on the coking chamber was 87,000 B.Th.U. per hour. In the circumstances the discrepancy between 102,000 B.Th.U. and 87,000 B.Th.U. is not excessive, and the figures indicate that practically all the heat transfer within the coking chamber was by radiation. This being the case, the width of the gap between the containers and the sides and bottom of the coking chamber is immaterial, provided that actual contact does not take place. The next step was therefore to calculate approximate heat input to the containers when they were in 100 per cent. contact with the bottom of the chamber, and also when the sides, too, were contacting. For these calculations the same values of the various heat constants were employed as for the preceding calculations. The conclusions only need be stated, viz:—

(1) The throughput of a coking plant with the lower surface of the buckets making 100 per cent. contact with the chamber is of the order of four times the throughput when the buckets merely slide into the chamber on runners.
(2) When both sides and bottom of the buckets are in contact with the coking chamber, the throughput is of the order of nine times that when the buckets are on runners.

Mechanical difficulties, however, render the touching of the sides and bottom impracticable, and the final plant was constructed with the buckets sliding into the chamber without runners, thereby making 100 per cent. contact at the bottom, and with a clearance between the buckets and the walls of the chamber of some 5 mm. on either side.

A further point of importance which arose as a result of the experimental investigation is the tremendous waste of heat involved in reheating the containers (after each cycle) from 130° C. to coking temperature. This requires more than 20 per cent. of the total heat input. Furthermore, the heating of the residue from 130° C. to coking temperature requires 41 per cent. of the total heat. In the designing of the full-scale plant, therefore, provision was made for keeping the whole chain of buckets totally enclosed, in order to reduce heat loss to the minimum. It was also decided to charge residue to the coking plant direct from the evaporators of the Kellogg stills, without any intermediate cooling. In this way the charge enters at a temperature of approximately 350° C., filling of the containers taking place in an atmosphere of steam.

In a subsequent publication it is proposed to deal with the construction

and operation of the actual working plant, and to give details of the throughputs, yields and types of products.

The Author's thanks are due to the Compañía Ferrocarrilera de Petroleo for permission to publish this paper, and he wishes to express his appreciation of the advice and assistance of Mr. E. P. Senior and Mr. G. H. May.

References.

[1] D. G. Jones, *J.I.P.T.*, 1935, **21**, 709.
[2] Staley, *Petr. Eng.*, 1932, **3** (5), 20.
[3] Foster, *Nat. Petr. News*, 1933, **25** (10), 26.
[4] Goldsbrough and Tevis, E.P. 320,619.
[5] Goldsbrough, U.S.P. 1,903,568.
[6] American Tar Products, E.P. 367,652.
[7] Moore, U.S.P. Re 19,104.
[8] Huff, U.S.P. 1,965,189.
[9] Richards and The Smokeless Fuel Syndicate, E.P. 15,933.
[10] Richards and Pringle, E.P. 15,643.
[11] Grondel and Carlson, E.P. 316,483.
[12] Möhring, E.P. 416,613.